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HULL UNIV (ENGLAND) DEPT OF CHEMISTRY

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KINETICS OF HYDROGEN-OXYGEN AND HYDROCARBON-OXYGEN REACTIONS. (U)

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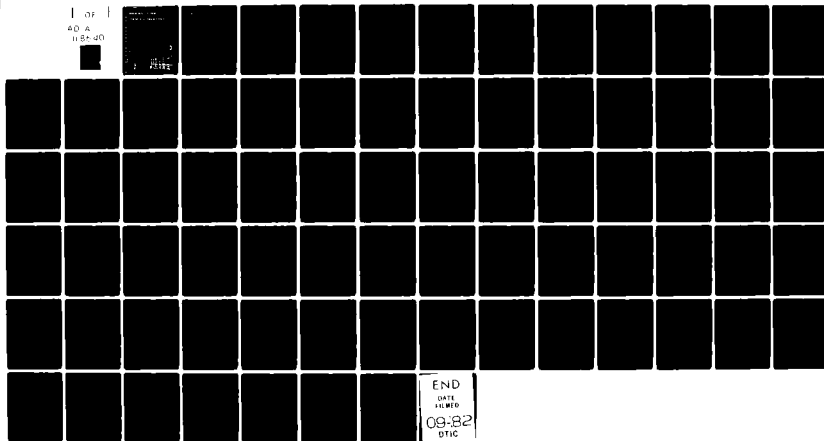
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BY R. R. BALDWIN & R. W. WALKER

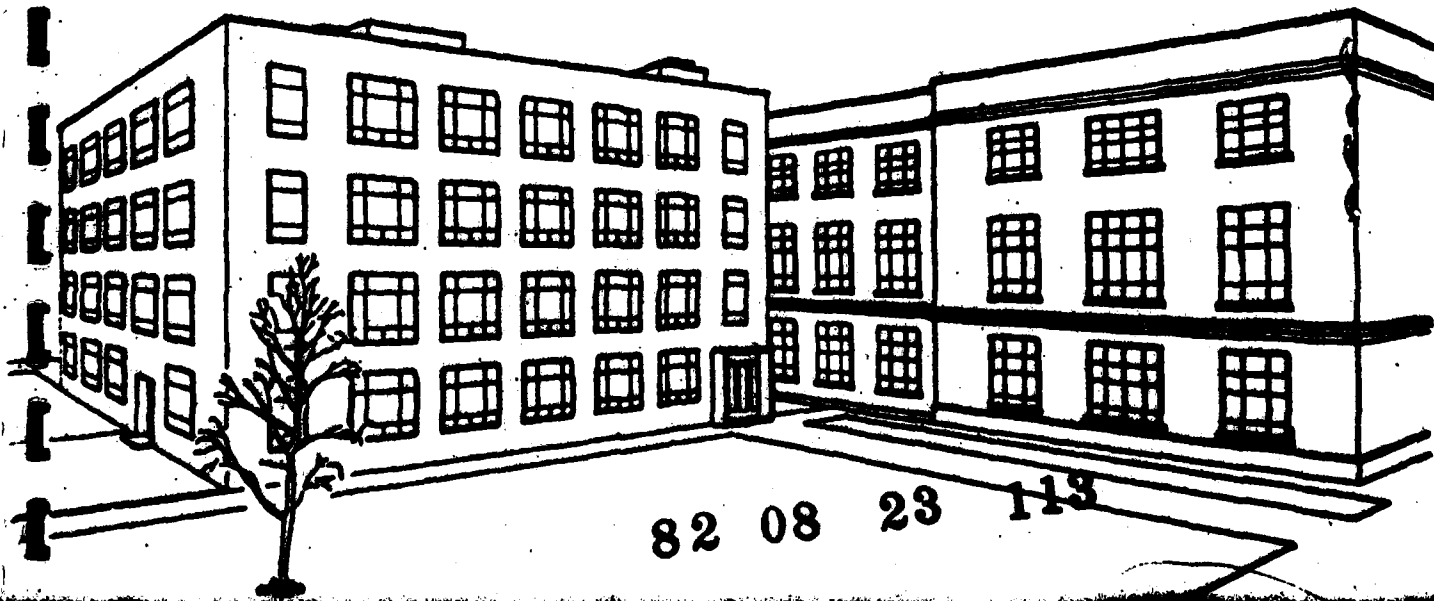
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) 1. Rate constants of the H₂ + O₂ reaction at 500 C have been refined. 2. Rate constants and Arrhenius parameters for reactions of H atoms and OH radicals with C₂-C₅ alkanes, 2,2,3,3-tetramethylbutane (TMB) and 2,2,3-trimethylbutane (TRIMB) have been obtained. Detailed studies have been made of the products from the oxidation of 1-butane, n-pentane, neopentane, TMB and TRIMB. Rate constants for R + O₂ = conjugate alkene, for homolysis of R Radicals, and for the isomerisation of RO₂ radicals to hydroperoxyalkyl radicals have been tabulated for a range of radicals. Preliminary studies have been made of the		

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oxidation process of alkenes. 4. Rate constants for reactions involved in the oxidation of propionaldehyde and of isobutyraldehyde have been listed. 5. The decomposition of TMB in the presence of O₂ has been used to study the reaction of HO₂ radicals with TMB, C₂H₆, C₂H₄, C₃H₆, and with CO, and the reaction of C₂H₅ and t-C₄H₉ radicals. 6. The decomposition of TRIMB in the presence of O₂ has enabled the thermochemistry of t-C₄H₉ and i-C₃H₇ radicals to be examined. 7. Interpretation of the N₂O and H₂ reaction has continued.

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Kinetics of Hydrogen-Oxygen and Hydrocarbon-Oxygen Reactions

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by Baldwin, R. R., and Walker, R. W.

Chemistry Department,
The University,
HULL.



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INTRODUCTION

The reaction of a hydrocarbon with oxygen is a complex process involving the formation of a large number of products which themselves influence the oxidation, particularly as they are usually more reactive than the parent material. As a consequence, the whole process is highly autocatalytic under many conditions, and the nature and concentration of the radicals vary sharply as the reaction proceeds. There are also regions where cool flames and ignition occur. These conditions are not suitable for the elucidation of the elementary reaction steps and evaluation of rate constants, as is illustrated by the very limited amount of quantitative information that has been obtained by direct studies of hydrocarbon oxidation despite the large number of investigations that have been made.

Over a number of years, the Hull group has been concerned with devising systems and conditions which permit the evaluation of the elementary steps in hydrocarbon oxidation. Three main approaches have been made.

1. The mechanism of the $H_2 + O_2$ reaction is well established in the temperature range around $500^{\circ}C$, and rate constants for the reactions involved have been determined accurately. The reaction thus forms a controlled environment in which to study the behaviour of an additive introduced in concentrations sufficiently small to avoid significant disturbance of the radical concentrations. Information can be obtained, first on the rate constants for the reaction of the radicals H and OH with the additive, and secondly on the reactions by which the radical formed from the parent material gives rise to the final products. The advantages of this approach are that the radical environment is under control, that a wide variety of additives can be made to undergo reactions at the same temperature, and that the intermediates believed to be important can be studied individually with the confidence that the radical environment is unaltered.

2. The oxidation of aldehydes in the range $150-300^{\circ}C$ is a complex process, in which peracids play an important role. At temperatures above $400^{\circ}C$, however, a much simpler mechanism operates, since the main products, an alkene and carbon monoxide, are much less reactive than the parent aldehyde, so that the complications inherent in the direct oxidation of alkanes do not

occur. The reaction is slightly autocatalytic due to dissociation of the reaction product, hydrogen peroxide, a fortunate situation that permits evaluation of the initiation rate for aldehyde + oxygen, and also enables the rate constant for HO_2 + aldehyde to be determined. The carbonyl radical RCO readily decomposes at these temperatures to $\text{R} + \text{CO}$, so that reactions of alkyl radicals can be studied.

3. Because of the strain in the central C-C link, the compounds 2,2,3,3-tetramethylbutane (TMB), and 2,2,3-trimethylbutane (TRIMB), decompose by C-C homolysis at temperatures much lower than most alkanes, and the rate of production of radicals by this process is faster by a factor of 10^2 to 10^3 than by the reaction of the hydrocarbon with oxygen, even at atmospheric pressure of oxygen. The decomposition is thus a source of t-butyl radicals in the case of TMB, and of t-butyl and i-propyl radicals in the case of TRIMB, thus enabling the reactions of these radicals to be studied. In the presence of oxygen, both these radicals react predominantly (99%) to give the HO_2 radical so that a convenient source of this radical over the temperature range 420-560°C is available.

These three approaches are complementary and all can be used to advantage in elucidating the complex processes involved in hydrocarbon oxidation. In many cases, simultaneous use of these methods has prevented wrong conclusions being drawn.

By use of these methods it has been shown that four main types of reaction account for the majority of initial products in alkane oxidation at 450-550°C.

- (a) Reaction of the alkyl radical with oxygen to form the conjugate alkene.
- (b) Decomposition of the alkyl radical to a lower alkene and a smaller alkyl radical.
- (c) Isomerisation of the alkylperoxy radical by internal hydrogen abstraction to form a hydroperoxyalkyl radical, which subsequently decomposes to give oxygenated ring compounds.
- (d) Reaction of the hydroperoxyalkyl radical with oxygen to give lower aldehydes and ketones.

A body of rate constants for these four types of reaction is being built up and the patterns involved are beginning to emerge. It should thus be

possible to use these patterns to provide rate constants for computer modelling of the initial stages of hydrocarbon oxidation for hydrocarbons which have not been studied experimentally. The possibility has already been examined in the case of n-pentane.

As already pointed out, alkenes are an early product of alkane oxidation, and a full computer modelling of hydrocarbon oxidation requires an understanding of the mechanism of alkene oxidation. This process is even more complex than alkane oxidation, since both radical addition and radical abstraction reactions are possible, and the full range of approaches already described will certainly be needed. Significant progress in understanding the processes involved has been made as a result of detailed studies of the addition of ethene and propene to slowly reacting mixtures of hydrogen and oxygen at about 500°C, and as a result of limited studies with the butenes and pentenes, made incidentally during investigations with the corresponding alkanes. Four main types of reaction appear to account for the main oxidation products from alkenes.

- (a) OH addition to the alkene, which appears to be the cause of the high aldehyde yields in alkene oxidation, though the exact mechanism remains uncertain.
- (b) HO₂ addition to the alkene, which accounts for the high yields of oxirans.
- (c) H addition to form a vibrationally-excited alkyl radical, which then decomposes completely or partially to a lower alkene and a lower alkyl radical.
- (d) H-abstraction from the alkene by the radicals H, OH and HO₂ to give an alkenyl radical. Virtually no information is available on the oxidation reactions of these radicals.

Details of individual studies are given in the following pages.

1. The hydrogen + oxygen reaction

Previously published rate constants for the very important elementary steps in the reaction between H_2 and O_2 have been evaluated with increased accuracy by allowing for the effect of self-heating in the system, the reaction of O atoms with hydrogen peroxide, and other minor refinements in the mechanism. The results indicate that, in most cases, the changes in the parameters due to the above effects are less than 10%, and the new values are summarised in Table 1 below.

Table 1
Rate Constant Ratios in $H_2 + O_2$ Reaction at 500°

$k_5/k_2k_{10}^{1/2}$	=	0.53	$(dm^3 mol^{-1}s^{-1})^{-1/2}$
$k_{8a}/k_2k_{10}^{1/2}$	=	0.081	$(dm^3 mol^{-1}s^{-1})^{-1/2}$
$k_{11}/k_{10}^{1/2}$	=	0.0366	$(dm^3 mol^{-1}s^{-1})^{-1/2}$
k_{14}/k_2	=	281	
k_{14a}/k_2	=	34	
k_{15}/k_1	=	4.5	
OH + H_2	→	H_2O + H	(1)
H + O_2	→	OH + O	(2)
H + HO_2	→	2OH	(3)
H + HO_2	→	H_2 + O_2	(3a)
HO_2 + HO_2	→	H_2O_2 + O_2	(4)
HO_2 + H_2	→	H_2O_2 + H	(5)
H + H_2O_2	→	H_2O + OH	(6)
H + H_2O_2	→	H_2 + HO_2	(6a)
OH + H_2O_2	→	H_2O + HO_2	(7)

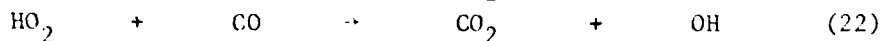
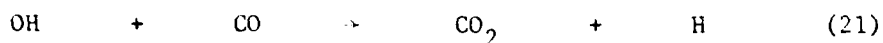
By use of the accurately known values of k_1 , k_2 and k_{10} , and by combining the present results with data at other temperatures, the Arrhenius expressions in Table 2 are recommended. Information in the literature on reactions (14) and (14a) at lower temperatures is conflicting, and the alternative interpretations are discussed in a recently published paper.¹

Table 2

Recommended Arrhenius Parameters for Reactions in $H_2 + O_2$ System

	$E/kJ\ mol^{-1}$	$A/(dm^3\ mol^{-1}\ s^{-1})$
$H + HO_2 \rightarrow 2OH$	7.6	5.4×10^{11}
$H + HO_2 \rightarrow H_2 + O_2$	0	2.8×10^{10}
$H + HO_2 \rightarrow H_2O + O$	7.6	5.5×10^{10}
$HO_2 + H_2 \rightarrow H_2O_2 + H$	90.0	2.0×10^9
$OH + H_2O_2 \rightarrow H_2O + HO_2$	4.8	3.7×10^9

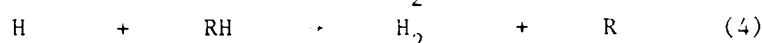
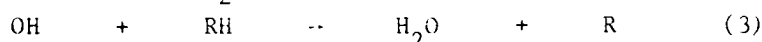
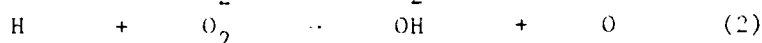
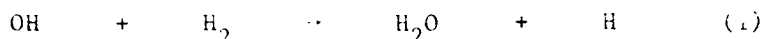
Studies of the addition of CO to slowly reacting mixtures of $H_2 + O_2$ have enabled values to be obtained for the rate constants for reactions of OH and HO_2 radicals with CO at $500^\circ C$. These reactions are of particular interest in the problem of atmospheric chemistry and automobile engine pollution, and conflicting values of k_{22} in particular have been published. Two types of study have been made, first the yields of CO_2 when small amounts ($\frac{1}{2}\%$) of CO are added, and secondly, the effect of large amounts of CO on the induction period and maximum rate of the slow reaction. Values of $k_{21}/k_1 = 0.235 \pm 0.02$, $k_{22}/k_{10}^{\frac{1}{2}} = 0.42 \pm 0.03$ ($dm^3\ mol^{-1}\ s^{-1}$) $^{\frac{1}{2}}$ have been obtained at $500^\circ C$, which combined with the accurately known values of k_1 , k_{10} , give $k_{21} = 0.96 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$, $k_{22} = 1.9 \times 10^4$. Arrhenius parameters $A_{22} = 5.8 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$, $E_{22} = 96.0\ kJ\ mol^{-1}$ are recommended. This work has been published.²



2. Addition of alkanes to slowly reacting mixtures of hydrogen and oxygen

(a) Rate constants for reaction of H atoms and OH radicals with alkanes

Results previously reported³ for the rate constants for reaction of H atoms and OH radicals with the hydrocarbons ethane, propane, n- and i-butane, and n- and neo-pentane have been re-examined to allow for the pressure changes due to the oxidation of the hydrocarbon, self-heating of the reaction mixture, and removal of the hydrocarbon by attack of O atoms and of HO₂ radicals. A computer treatment has enabled all these complications to be analysed. Although no single factor has a major effect, the combined effect is to reduce the rate constant for OH attack by a factor of approximately 2, whereas the value for H attack is almost unaltered.



Examination of the results indicates that the total rate constant for radical attack on an alkane can be obtained by summing the contributions from attack at the three different types of C-H bond, primary, secondary and tertiary, in the molecule. Combination with data by Greiner⁴ at lower temperatures for OH attack enables the Arrhenius parameters A_3/A_1 and $(E_1 - E_3)$ to be obtained for each type of bond. The data for C₂-C₅ alkanes are self-consistent, and examination indicates that the overall rate constant ratio k_3/k_1 can be expressed by equation (i).

$$k_3/k_1 = 0.214n_p \exp(1070/T) + 0.173n_s \exp(1820/T) + 0.273n_t \exp(2060/T) \quad (i)$$

where n_p , n_s and n_t are the number of primary, secondary and tertiary C-H bonds in the molecule. Similar treatment of the data for H atoms gives the expression (ii) for the ratio k_4/k_2 at 480°C.

$$k_4/k_2 = 7.0n_p + 43n_s + 160n_t \quad (ii)$$

Absolute values of k_3 and k_4 can be obtained by substituting the known values of k_1 and k_2 in expressions (i) and (ii). By fitting a slight curve to the points obtained by Greiner,⁵ by Eberius et al.,⁶ and by Westenberg and de Haas,⁷ Baldwin and Walker¹ give $k_1 = 1.28 \times 10^5 T^{1.5} \exp(-1480/T)$

$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ over the temperature range 300-900 K. The best value of k_2 at 480°C is obtained by combining the ratio $k_4/k_2 = 44$ for ethane from addition studies with Camilleri, Marshall and Purnell's expression⁸ $k_4 = 1.32 \times 10^{11} \exp(-4715/T)$, giving $k_2 = 5.7 \times 10^6 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$. Data on rate constants at other temperatures are more limited for H than for OH, but on the basis of the data available, the following Arrhenius parameters are recommended.

Table 3
Arrhenius Parameters for H Abstraction by H Atoms from Alkane

Type of bond	$E_4/\text{kJ mol}^{-1}$	A_4 per C-H bond $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
primary	39.2	2.2×10^{10}
secondary	33.3	4.9×10^{10}
tertiary	25.2	5.1×10^{10}

To deduce the mechanism of product formation in alkane oxidation, it is necessary to know the proportions of the various radicals formed by H and OH attack on the alkane, and equations (i) and (ii) provide the best available method. However, this procedure may be less reliable if there is a high degree of branching in the molecule. This is shown by some experimental studies recently made⁹ with 2,2,3,3-tetramethylbutane as additive. The rate constant ratios k_3/k_1 and k_4/k_2 at 480°C are given below for this hydrocarbon and for neopentane and ethane, which also contain only primary C-H bonds.

Table 4
Rate Constant Ratios for H + RH and OH + RH at 480°C

Hydrocarbon	k_3/k_1	k_4/k_2
ethane	5.7 ± 0.5	44 ± 4
neopentane	10.0 ± 1.0	52 ± 5
tetramethylbutane	8.0 ± 1.0	112 ± 8

On a simple additivity basis, these results should each be in the ratio 1:2:3.

Use of the values of k_3/k_1 for the three alkanes with $k_1 = 1.28 \times 10^5 T^{1.5} \exp(-1480/T)$ gives the absolute values of k_3 . When combined with Greiner's⁴ low temperature data, good Arrhenius plots may be drawn for all three alkanes over the temperature range 300 - 750 K giving the Arrhenius parameters summarised in Table 5. There appear to be systematic changes in both the values of the A factors and of the activation energies as the degree of branching in the alkanes increases, so that kinetic predictions based on bond additivity must be used with caution when applied to branched alkanes.

Table 5
Arrhenius Parameters for OH attack at Primary C - H Bonds

Alkane	E/kJ mol ⁻¹	A (overall)/ (dm ³ mol ⁻¹ s ⁻¹)	A (per C - H bond)/ (dm ³ mol ⁻¹ s ⁻¹)
CH ₃ CH ₃	10.0 ± 0.6	(1.07 ± 0.18) × 10 ¹⁰	(1.78 ± 0.30) × 10 ⁹
C(CH ₃) ₄	8.7 ± 0.8	(1.55 ± 0.26) × 10 ¹⁰	(1.29 ± 0.22) × 10 ⁹
(CH ₃) ₃ CC(CH ₃) ₃	6.6 ± 0.6	(9.45 ± 2.0) × 10 ⁹	(5.25 ± 1.1) × 10 ⁸

Recent work with 2,2,3-trimethylbutane gives $k_3/k_1 = 12.2 \pm 1.5$ and $k_4/k_2 = 257 \pm 10$ at 480°C. These may be compared with the values of 17.5 and 265, calculated from expressions (i) and (ii). Use of independent data for k_1 and k_2 gives $k_3 = 4.5 \times 10^9$ and $k_4 = 1.48 \times 10^9$ dm³ mol⁻¹ s⁻¹. Combination with Greiner's low temperature results gives $A_3 = (5.9 \pm 0.5) \times 10^9$ dm³ mol⁻¹ s⁻¹ and $E_3 = 1800 \pm 300$ J mol⁻¹. This work has been accepted for publication.¹⁰

The results in Table 4 suggest that the method used to obtain the values for the tertiary C-H bond in equations (i) and (ii) should be slightly refined. The values for k_3^t/k_1 , k_4^t/k_2 have thus been obtained from $k_3/k_1 = 12.2$, $k_4/k_2 = 257$ by subtracting the contribution for fifteen primary C-H bonds using the value per primary C-H bond obtained from k_3/k_1 , k_4/k_2 for tetramethylbutane. The values of $k_3^t/k_1 = 5.5$, $k_4^t/k_2 = 164$ are in close agreement with values of 5.0, 184 respectively using the values of k_3/k_1 , k_4/k_2 for isobutane and allowing for the contribution of primary C-H bonds using the values of k_3/k_1 , k_4/k_2 given in Table 4 for neopentane. By combining the present value of k_3^t (calculated from the known value of k_1) obtained from 2,2,3-trimethylbutane and 2,2,3,3-tetramethylbutane with the values given by Greiner,⁴ treated in the same way, $\log_{10}(A_3^t/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 9.23 \pm 0.10$, $E_3^t = -960 \pm 800$ J mol⁻¹. Alternatively, use of the values for

isobutane and neopentane gives $\log_{10}(A_3^t/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 9.41 \pm 0.10$, $E_3^t = 2250 \pm 800 \text{ J mol}^{-1}$. The reason for the difference in these two sets of parameters, which has its origin in Greiner's results since the two sets of values of k_3^t/k_1 are within 10% at 480°C , is not clear. From the mean line through the $\log k_3^t$, $1/T$ plots for i-butane and 2,2,3-trimethylbutane, $\log_{10}(A_3^t/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 9.32 \pm 0.10$, $E_3^t = 460 \pm 950$, and these parameters are recommended for general use with alkanes in the temperature range 300-1500 K.

In an effort to clarify the position concerning attack at the tertiary C - H bond, studies of the addition of 0.025% of 2,3-dimethylbutane to slowly reacting mixtures of $\text{H}_2 + \text{O}_2$ at 480°C have just been completed. As expected, because of the presence of two tertiary C - H bonds, the results suggest that the overall rate constants for H and OH attack on the alkane are slightly higher than those for 2,2,3-trimethylbutane. A final, precise interpretation of the results awaits a detailed study of the products formed from 2,3-dimethylbutane, and this investigation is in progress.

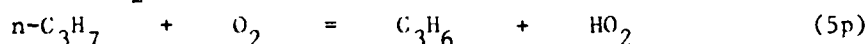
(b) Reactions of alkyl radicals

The second object of studies of the addition of small amounts of an alkane to slowly reacting mixtures of $H_2 + O_2$ is to obtain information on the reactions of the radicals produced from the alkane, and the mechanism of formation of the various products. The advantages of this approach over direct studies of alkane oxidation have been discussed elsewhere, and include the fact that the radical concentration is controlled by the $H_2 + O_2$ system rather than the alkane, the fact that a wide range of concentrations can be investigated under essentially identical conditions, and that primary and secondary products can easily be distinguished.

Studies with a range of alkanes have clarified considerably the mechanism of oxidation and suggested that the main initial products in alkane oxidation at temperatures around $500^\circ C$ result from four major types of reaction.

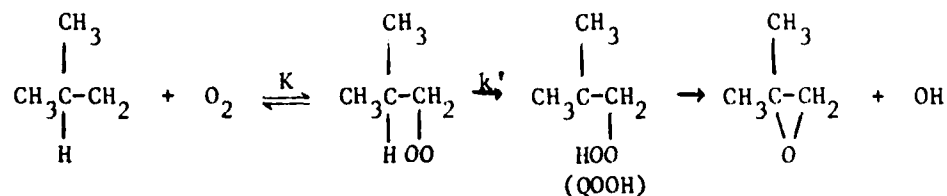
(i) Decomposition of the alkyl radical to a lower alkene and a smaller alkyl radical.

(ii) Formation of conjugate alkenes by the reaction of the alkyl radical with O_2 , for example:



Although this reaction may occur through addition of O_2 to the alkyl radical to form the RO_2 radical, followed by decomposition to give the alkene + HO_2 , this path is kinetically identical to reaction (5p), since R and RO_2 are almost always equilibrated, and the bimolecular form (5p) is preferred.

(iii) Addition of O_2 to form the RO_2 radical followed by isomerisation to give a peroxyalkyl radical ($QOOH$) and decomposition to give an oxygen-ring compound. This is illustrated by the formation of isobutene oxide from isobutyl radicals.



As shown in previous papers, the overall rate constant for this reaction is given by expression (iii)

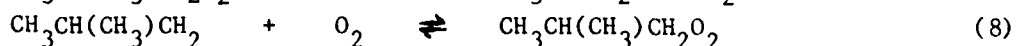
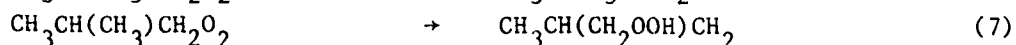
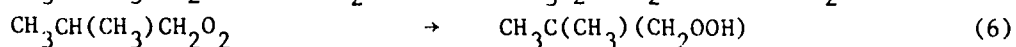
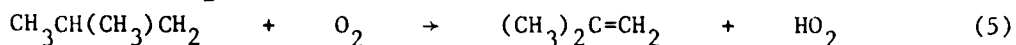
$$k = Kk' \quad (iii)$$

where K is the equilibrium constant for the $R + O_2 = RO_2$ equilibrium.

(iv) Reaction of the peroxyalkyl radical (QOOH) with O_2 to give oxygenated products, such as aldehydes and ketones.

With the completion of studies, now published,¹¹ with i-butane as additive, rate constants for a number of specific radicals giving specific alkenes have been obtained, and these are summarised in Table 6. Interpretation of the results from i-butane was facilitated by studies, described in section (5), of the decomposition of tetramethylbutane in the presence of O_2 which showed that 99% of the t-butyl radicals formed react with O_2 to give i-butene and the remaining 1% react with O_2 to give isobutene oxide. The residual products from i-butane addition are thus formed solely from the i-butyl radical. The advisability of using a multi-channelled approach in solving the problems associated with hydrocarbon oxidation is thus emphasised again.

The studies with i-butane have been particularly important in two respects. First, a value of $k_5 = 6.8 \times 10^7$ has been obtained which, when combined with a low temperature measurement gives $A_5 = 6.9 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $E_5 = 29 \text{ kJ mol}^{-1}$. No other determinations of the Arrhenius parameters for conjugate alkene formation exist. From measurements of the relative yields of isobutene oxide and 3-methyloxetan, a value of $k_6/k_7 = 4.1 \pm 0.4$ is obtained. Use of the rather uncertain value of the rate constant for the decomposition of i-butyl radicals, together with the best thermochemical data available for reaction (8), gives $k_6 = 1.83 \times 10^5 \text{ s}^{-1}$, $k_7 = 4.45 \times 10^4 \text{ s}^{-1}$ at 480°C . No other experimental value is available for k_6 nor for any similar reaction involving the transfer of a tertiary H atom. Rate constants for the isomerisation of RO_2 radicals to QOOH radicals are summarised in Table 7.



A summary of all the rate constants obtained by the study of i-butane as additive is given in Appendix I.

A complete analysis of the products when the highly branched alkane 2,2,3,3-tetramethylbutane (TMB) is the additive has been made at 480°C over a wide range of mixture composition. Isobutene in about 95% yield is the only major initial product, although small amounts (ca. 1%) of propene, 2,3,3-trimethylbutene-1, isobutene oxide, formaldehyde and methane are also formed. No evidence has been found for the presence of O-ring compounds containing the same number of carbon atoms as TMB. Thus, even at pressures of O_2 approaching atmospheric, the TMB radical $((\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_2\text{CH}_2)$ breaks down almost completely by the dissociation reaction (9) at 480°C . By measuring the yields of (propene + 2,3,3-trimethylbutene-1) relative to i-butene as a function of O_2 concentration, the ratio k_9/k_{10} has been obtained. From a reasonable estimate of k_{10} , based on analogous

Table 6
Rate Constants for Formation of Alkenes and Dienes
at 480°C

Radical	Type of CH Bond	Product	k $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ per C-H bond	ΔH kJ mol^{-1}
$\underline{\text{CH}_3}\text{CH}_2$	Primary	C_2H_4	6.6×10^7	2.2×10^7	-45.0
$\text{CH}_3\text{CH}\underline{\text{CH}}_3$	Primary	C_3H_6	1.3×10^8	2.1×10^7	-39.8
$\text{CH}_3\text{CHCH}_2\underline{\text{CH}}_3$	Primary	C_4H_8-1	5.1×10^7	1.7×10^7	-37.5
$\text{CH}_3\underline{\text{CH}_2}\text{CH}_2$	Secondary	C_3H_6	7.1×10^7	3.6×10^7	-53.5
$\text{CH}_3\text{CH}_2\underline{\text{CH}_2}\text{CH}_2$	Secondary	C_4H_8-1	1.6×10^8	8.0×10^7	-55.5
$\text{CH}_3\text{CHCH}_2\underline{\text{CH}}_3$	Secondary	C_4H_8-2 (trans)	7.8×10^7	3.9×10^7	-49.0
		C_4H_8-2 (cis)	4.3×10^7	2.2×10^7	-45.0
$(\text{CH}_3)_2\underline{\text{CH}}\text{CH}_2$	Tertiary	i- C_4H_8	6.8×10^7	6.8×10^7	-61.5
$\text{CH}_2\underline{\text{CHCHCH}_2}\text{CH}_3$	-	$\text{CH}_2=\text{CHCH}=\text{CHCH}_3$	2.1×10^6	1.05×10^6	-14.0

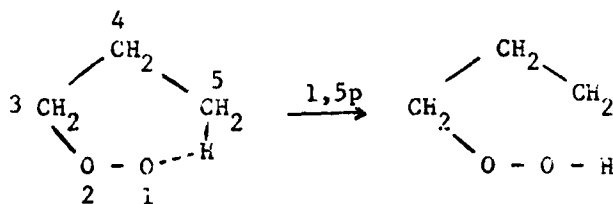
The underlined H atom indicates the site of removal.

Table 7

Rate Constants for the formation of QOOH Radicals

C-H bond broken	Type of H atom transfer ^a	k/s ⁻¹ at 480°C	E ^b /kJ mol ⁻¹
primary	1,3p	(1.3 x 10 ¹) ^c	159
	1,4p	2.2 x 10 ³	125
	1,5p	1.8 x 10 ⁴	110
	1,6p	6.0 x 10 ⁴	105
	1,7p	9.3 x 10 ⁴	102
secondary	1,3s	(1.4 x 10 ²)	144
	1,4s	2.4 x 10 ⁴	111
	1,5s	3.0 x 10 ⁵	95
	1,6s	(6.5 x 10 ⁵)	90
tertiary	1,3t	1.5 x 10 ³	130
	1,4t	1.8 x 10 ⁵	98
	1,5t	(2.2 x 10 ⁵)	8-
	1,6t	(7.1 x 10 ⁶)	75

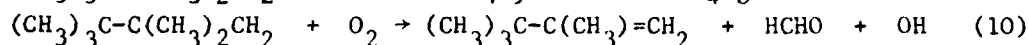
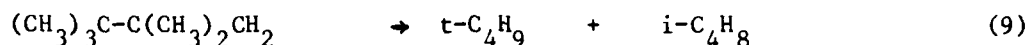
^a In this table, p, s, t refer to abstraction from primary, secondary and tertiary C-H bonds, and the adjacent numbers refer to the position of the atom abstraction as illustrated below for a 1,5p transition.



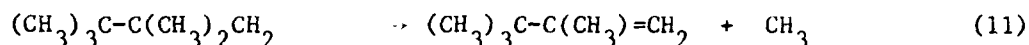
^b Calculated using $A = 10^{12.1} \text{ s}^{-1}$, the value suggested by Benson for a 1,5 transfer. It has been suggested, however, that the value of A decreases as the ring size increases.

^c Values in brackets are estimates, based on the experimental values.

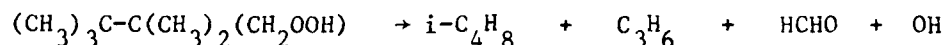
reactions,* $k_9 = 1.9 \times 10^6 \text{ s}^{-1}$ at 480°C . This value is a factor of 10-100 times greater than the values of rate constants for the C-C homolysis of $n\text{-C}_3\text{H}_7$, $s\text{-C}_4\text{H}_9$, $i\text{-C}_4\text{H}_9$ and $\text{neo-C}_5\text{H}_{11}$ radicals, presumably because of the considerable strain in the central C-C bond in the TMB radical.



From the yields of 2,3,3-trimethylbutene-1, the rate constant k_{11} has been obtained as $1.1 \times 10^4 \text{ s}^{-1}$, close to the expected value for loss of a methyl radical by C-C homolysis. No rate constants for the decomposition processes k_9 and k_{11} were previously available.



In the case of propylperoxy, neopentylperoxy and all four species of butylperoxy radical, the hydroperoxyalkyl radicals (QOOH) formed by internal H-atom transfer, either decompose by loss of OH and then cyclise to give an O-ring compound, or add a further molecule of O_2 before decomposing. No evidence has been found for either of these types of reaction in the case of the QOOH radical formed from tetramethylbutylperoxy radicals, and it appears to react uniquely by β - and γ -scission to give lower alkenes, as illustrated by the reaction below.

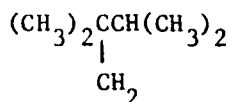


The shift to C-C scission reactions in the case of QOOH radicals formed from TMB must thus be associated with the steric strain in the central C-C bond.

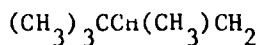
This work has now been published⁹ and the rate constants obtained are summarised in Table 8.

A detailed study¹⁰ has been made over a wide range of mixture composition using 2,2,3-trimethylbutane (TRIMB) as additive; rate constants for H and OH attack on this alkane have been discussed in section (a). The mechanism of product formation is considerably more complex than that for TMB because three different species, A, B, and C, are formed by radical attack on TRIMB.

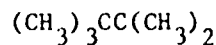
* Reaction (10), though represented kinetically by the equation given, proceeds through formation of the peroxyradical, isomerisation to a peroxyalkyl radical, and subsequent decomposition, as already discussed.



(A)



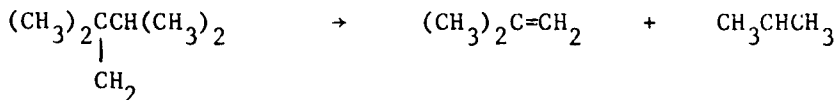
(B)



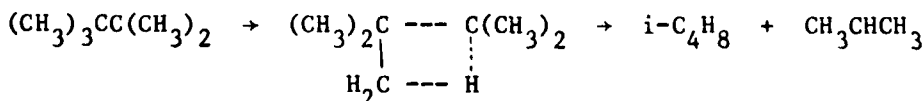
(C)

As a necessary pre-requisite to quantitative interpretation, by using the additivity principle expressed by equations (i) and (ii), the proportions of the three radicals formed may be calculated. For the standard mixture, $\text{O}_2 = 70$, $\text{H}_2 = 140$, $\text{N}_2 = 285$, TRIMB = 5 Torr at 480°C , the initial yields are $A = 18.5\%$, $B = 12.5\%$, and $C = 69\%$, with little change in the proportions as the mixture composition is varied.

Product analysis shows that the major initial products are isobutene and propene, formed in nearly equal amounts (about 80% of TRIMB consumed for the above mixture), and 2,3,3-trimethylbutene-1 (13%), with lower alkenes, formed by CH_3 loss from radicals A, B, and C, as minor products. The yield of 2,3,3-trimethylbutene-1 increases markedly with increase in the pressure of O_2 . It is concluded from a detailed analysis of the results that radicals A and B predominantly undergo homolysis of the strained central C - C bond.



Although previous studies have established that 99% of t-butyl and isopropyl radicals react with O_2 to give isobutene and propene, respectively, under the conditions used, it is clear that radical C must be a major source of these alkenes. After allowance for formation from radicals A and B, the relative rate of formation of isobutene (from C) and 2,3,3-trimethylbutene-1 is inversely proportional to the pressure of O_2 . As radical C cannot undergo a simple homolysis of the central C - C bond without H atom transfer, which would be very slow, it is suggested that C decomposes into isobutene and isopropyl radicals in a concerted mechanism.



The oxygen dependence provides strong support for the formation of

2,3,3-trimethylbutene-1 in the following reaction.



Rate constants have been obtained for the concerted reaction of radical C and for the various homolyses of radicals A and B, and the values are summarised in Table 8, together with values for the decomposition of related radicals obtained in a similar manner. The values in Table 8 have not previously been determined, and this is indicative of the general lack of rate data for elementary combustion reactions involving alkyl radicals containing more than five carbon atoms.

Measurements at temperatures significantly different from 480°C were not possible, but activation energies may be calculated from estimates of the A factors for the homolyses. From transition state theory, $A = (ekT/h)e^{\Delta S^\ddagger/R}$, so that A is effectively determined by the values of ΔS^\ddagger . Various arguments may be advanced for a value of $\Delta S^\ddagger \sim 4 \text{ J K}^{-1} \text{ mol}^{-1}$ for all the homolyses, so that A is estimated as $10^{13.8 \pm 0.5} \text{ s}^{-1}$ at 480°C. Combination of this value with the rate constant of each homolysis at 480°C gives the activation energies shown in Table 8, the accuracy specified being due to the uncertainty in the value of A.

A full analysis of the reaction products has also been made with n-pentane as additive. Details of the product distribution have been given in an earlier report and in published papers.^{12,13} At the time of the study, no specific rate constants, except for H and OH attack on pentane, were available for any of the elementary reactions involved in the system. However, by use (without modification) of rate constants obtained from studies with C₂ - C₄ alkanes and neopentane, it is possible to predict the initial yields of the major products (accounting for 95% consumed) from pentane to better than a factor of 2 over a wide range of mixture composition. The possibility, applied here, of the general use of rate constants determined for specific reactions is of great importance to computer modelling of complex systems, where it is extremely unlikely that a major proportion of the rate constants is known accurately.

Although showing only minor changes from those used above, accurate rate constants for the specific elementary reactions in the pentane system may be obtained from a quantitative treatment of the results. Use of the rate constants for attack of H, OH, and HO₂ at specific C - H bonds in pentane

Table 8

Decomposition of Alkyl Radicals at 480°C

Reaction	$\Delta U/\text{kJ mol}^{-1}$	k/s^{-1}	$E_f/\text{kJ mol}^{-1}$ ($A = 10^{13.8 \pm 0.5} \text{ s}^{-1}$)
$(\text{CH}_3)_3\text{CC}(\text{CH}_3)_2 \rightarrow (\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2 + \text{CH}_3$	115 ± 4	7.2×10^2	158 ± 7
$(\text{CH}_3)_3\text{CCH}(\text{CH}_3)\text{CH}_2 \rightarrow (\text{CH}_3)_3\text{CCH}=\text{CH}_2 + \text{CH}_3$	84 ± 4	6.2×10^4	130 ± 7
$(\text{CH}_3)_3\text{CCH}(\text{CH}_3)\text{CH}_2 \rightarrow \text{t-C}_4\text{H}_9 + \text{C}_3\text{H}_6$	51 ± 4	1.3×10^6	111 ± 7
$(\text{CH}_3)_2\text{C}(\text{CH}_2)\text{CH}(\text{CH}_3)_2 \rightarrow \text{CH}_2=\text{C}(\text{CH}_3)\text{CH}(\text{CH}_3)_2 + \text{CH}_3$	77 ± 4	2.4×10^5	121 ± 7
$(\text{CH}_3)_2\text{C}(\text{CH}_2)\text{CH}(\text{CH}_3)_2 \rightarrow \text{i-C}_3\text{H}_7 + (\text{CH}_3)_2\text{C}=\text{CH}_2$	59 ± 4	2.4×10^6	107 ± 7
$(\text{CH}_3)_3\text{CC}(\text{CH}_3)_2^* \rightarrow \text{i-C}_3\text{H}_7 + (\text{CH}_3)_2\text{C}=\text{CH}_2$	92 ± 4	7.4×10^5	114 ± 7
$(\text{CH}_3)_3\text{CC}(\text{CH}_3)_2\text{CH}_2 \rightarrow \text{t-C}_4\text{H}_9 + (\text{CH}_3)_2\text{C}=\text{CH}_2$	36 ± 4	1.9×10^6	108 ± 7
$(\text{CH}_3)_3\text{CC}(\text{CH}_3)_2\text{CH}_2 \rightarrow (\text{CH}_3)_3\text{CC}(\text{CH}_3)=\text{CH}_2 + \text{CH}_3$	70 ± 4	1.1×10^4	140 ± 7
$\text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{CH}_3$	100 ± 4	1.6×10^5	124 ± 7
$\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{C}_3\text{H}_6 + \text{C}_2\text{H}_5$	92 ± 4	2.3×10^5	122 ± 7

* A concerted mechanism involving an H atom transfer is suggested for this reaction (see text)

enables the proportions of 1-pentyl, 2-pentyl, and 3-pentyl radicals to be calculated for all the mixtures used. By use of a wide range of H_2 , and particularly, of O_2 (8 - 355 Torr) pressures it is possible to confirm suggested mechanisms for the oxidation of each of the three species of pentyl radical. Rate constants have been obtained for the first time for a large number of the elementary reactions involved, and the values form a very consistent pattern with those determined from studies with the $C_2 - C_4$ alkanes and neopentane as additive. Rate constants for the pentane system are summarised in Appendix II.

Previous studies of the addition of neopentane to slowly reacting mixtures of $H_2 + O_2$ at $480^\circ C$ have permitted the elucidation of the elementary reactions involved in the formation of O-heterocyclic and other oxygenated products. Two particular features of neopentane facilitate simple interpretation of the results.

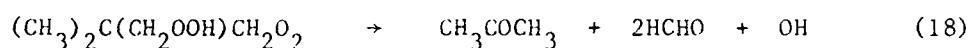
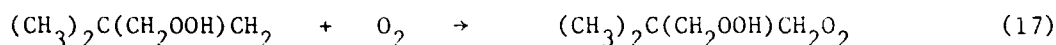
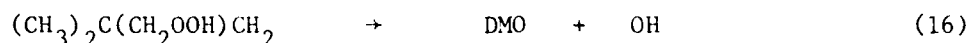
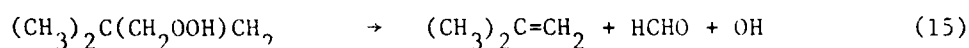
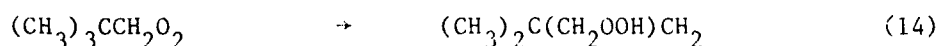
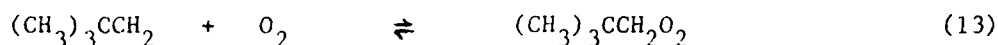
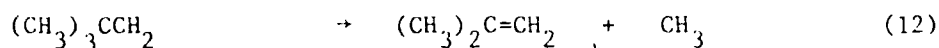
- (i) All the C - H bonds are identical, so that only one species of alkyl radical is involved.
- (ii) Unlike the majority of simple alkyl radicals, where reaction with O_2 to form the conjugate alkene is the dominating process over the temperature range $300 - 550^\circ C$, such a reaction is structurally impossible for the neopentyl radical so that reactions, normally of minor importance with other radicals, are dominant.

With the acquisition of more sophisticated and sensitive gas chromatography equipment, sufficient accuracy of analysis was available to permit determination of the Arrhenius parameters of the elementary reactions involved in the neopentane system.

Detailed product analyses were carried out using a basic mixture containing 5 Torr of neopentane, 140 Torr of H_2 , and variable pressures of O_2 at a fixed total pressure (usually 500 Torr) by use of added N_2 . Over a wide range of mixture composition and at total pressures between 250 and 600 Torr, the only major initial products between 380 and $520^\circ C$ were methane, formaldehyde, 3,3-dimethyloxetan (DMO), acetone, and i-butene, which collectively accounted for at least 98% of the neopentane consumed in the early stages of reaction.

A relatively simple mechanism involving the formation of neopentyl-hydroperoxide (QOOH) radicals gives a quantitative interpretation of the product yields under all conditions used. Although, as expected, the major source of i-butene is the C - C homolysis of the neopentyl radical (12), a

significant proportion is formed in the direct homolysis of the QOOH radical.



Methane and formaldehyde are formed by reaction of CH_3 radicals with H_2 and O_2 , respectively, and these reactions will not be discussed here.

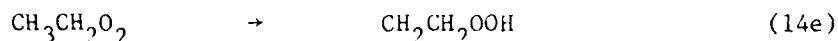
From measurements of the product ratios $([\text{acetone}] + [\text{DMO}])/[\text{i-butene}]$ and $[\text{acetone}]/[\text{DMO}]$ over a wide range of O_2 pressure at 380, 400, 440, 480, 500, and 520°C, Arrhenius parameters have been obtained for a number of the elementary steps. The values are summarised in Table 9, and are based on a value of $k_{12} = 4.45 \times 10^{13} \exp(-127500 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$; no other values are available for these reactions.

Table 9
Arrhenius Parameters for Elementary Steps in the Neopentane + O_2 System

Reaction	A/s^{-1}	$E/\text{kJ mol}^{-1}$
(14)	1.2×10^{13}	120
(15)	4.5×10^{13}	116
(16)	2.0×10^{11}	73
(18)	1.25×10^{12}	96.5

The kinetic data for the 1,5p H atom transfer in reaction (14) may be compared with the only other experimental parameters available for a similar process, namely the 1,4p transfer in reaction (14e), for which the values $A_{14e} = 10^{13.3 \pm 0.6} \text{ s}^{-1}$ and $E_{14e} = 144.0 \pm 10 \text{ kJ mol}^{-1}$ have been obtained over the temperature range 400 - 540°C (section 5d). The difference in the values of the activation energies is entirely in agreement with the expected difference in the strain energies involved in the formation of the two ring transition states, and the ratio of A factors on a per C - H

bond basis is in quantitative agreement with transition state theory predictions concerning the increasing loss of entropy of activation as the size of the ring transition state increases.



Using the kinetic data for reaction (14) as a basis, Arrhenius parameters for other H atom transfers (Table 7) have been estimated from values of rate constants determined only at 480°C. Transition state theory predicts that the calculated A factor per C - H bond available for the transfer should decrease by a factor of 8 each time the size of the ring transition state is increased by one atom. The calculations are summarised in Table 10. The values represent the most comprehensive assembly of data available for this type of reaction.

This work has been submitted for publication.¹⁴

Preliminary studies have been made with 2,3-dimethylbutane as additive. The major initial products are the two conjugate alkenes, 2,3-dimethylbutene-2 and 2,3-dimethylbutene-1, and the homolysis products methane, propene, and 2-methylbutene-2, together with smaller amounts of other products including 2,2,3,3-tetramethyloxiran. Simple schemes may be written for the formation of all the named products, and it should be possible to determine rate constants for a number of the elementary processes involved.

Table 10

Arrhenius Parameters for H atom transfer reactions in RO₂ Radicals

Reaction	Type	k/s ⁻¹	k/s ⁻¹ (per C - H)	A/s ⁻¹ (per C - H)	E/kJ mol ⁻¹	E/kJ mol ⁻¹ (for type)
CH ₃ CH ₂ CH(OO)CH ₃ → CH ₃ CH ₂ CH(OOH)CH ₃	1,4p	2.2 × 10 ³	7.3 × 10 ²	8 × 10 ¹²	144.8	145
CH ₃ CH ₂ OO → CH ₂ CH ₂ OOH*	1,4p	1.95 × 10 ³	6.5 × 10 ²	8 × 10 ¹²	145.5	
(CH ₃) ₂ CHCH ₂ OO → (CH ₃) ₂ C(CH ₂ OOH)CH ₂ *	1,5p	9.2 × 10 ⁴	1.02 × 10 ⁴	1.0 × 10 ¹²	115.2	117
	1,5p	5.7 × 10 ⁴	6.3 × 10 ³	1.0 × 10 ¹²	118.2	
	1,5p	4.45 × 10 ⁴	7.4 × 10 ³	1.0 × 10 ¹²	117.2	
(CH ₃) ₂ C(H)CH ₂ OO → CH ₃ C(H)(CH ₂ OOH)CH ₂	1,6p	6.0 × 10 ⁴	2.0 × 10 ⁴	1.25 × 10 ¹¹	97.9	98
CH ₃ CH ₂ CH ₂ CH ₂ OO → CH ₂ CH ₂ CH ₂ CH ₂ OOH	1,7p	9.3 × 10 ⁴	3.1 × 10 ⁴	1.55 × 10 ¹⁰	82.1	82
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OO → CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OOH	(1,3s)			(6.4 × 10 ¹³)	(168)*	
CH ₃ CH(OO)CH ₂ CH ₃ → CH ₃ CH(OOH)CHCH ₃	1,4s	2.4 × 10 ⁴	1.2 × 10 ⁴	8 × 10 ¹²	127.2	125
CH ₃ CH(OO)CH ₂ CH ₂ CH ₃ → CH ₃ CH(OOH)CHCH ₂ CH ₃	1,4s	4.7 × 10 ⁴	2.35 × 10 ⁴	8 × 10 ¹²	123.0	
CH ₃ CH ₂ CH ₂ CH ₂ OO → CH ₃ CHCH ₂ CH ₂ OOH	1,5s	2.0 × 10 ⁵	1.0 × 10 ⁵	1.0 × 10 ¹²	100.9	100
CH ₃ CH(OO)CH ₂ CH ₂ CH ₃ → CH ₃ CH(OOH)CH ₂ CHCH ₃	1,5s	3.0 × 10 ⁵	1.5 × 10 ⁵	1.0 × 10 ¹²	98.4	
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OO → CH ₃ CHCH ₂ CH ₂ CH ₂ OOH	1,6s	6.6 × 10 ⁵	3.3 × 10 ⁵	1.25 × 10 ¹¹	80.4	80
	(1,7s)			(1.55 × 10 ¹⁰)	(64)*	
CH ₃ CH(OO)CH ₂ CH ₃ → CH ₃ C(OOH)CH ₂ CH ₃	1,3t	1.5 × 10 ³	1.5 × 10 ³	6.4 × 10 ¹³	153.3	153
(CH ₃) ₂ CHCH ₂ OO → (CH ₃) ₂ CCH ₂ OO	1,4t	1.83 × 10 ⁵	1.83 × 10 ⁵	8 × 10 ¹²	110.2	110

Table 10(cont)

Reaction	Ref	Type	k/s ⁻¹	k/s ⁻¹ (per C - H)	A/s ⁻¹ (per C - H)	E/kJ mol ⁻¹	E/kJ mol ⁻¹ (for type)
		(1,5t)			(1.0 × 10 ¹²)	(84) ⁺	
		(1,6t)			(1.25 × 10 ¹¹)	(64) ⁺	
		(1,7t)			(1.55 × 10 ¹⁰)	(48) ⁺	

Footnotes

- * Experimentally determined Arrhenius parameters for these reactions are discussed in the text.
- + Activation energies given in brackets are calculated on the assumption that the differences in the activation energies for the transfer of a particular type of H atom (say primary) are due to differences in the strain energies in the ring transition states. Thus, for example, $E(1,3s) = E(1,4s) + E(1,3t) - E(1,4t)$.

3. Addition of alkenes to slowly reacting mixtures of hydrogen and oxygen

Previous studies of the addition of alkanes to slowly reacting mixtures of $H_2 + O_2$ have shown that conjugate and lower alkenes are the major primary products, sometimes in yields of over 80%, in the oxidation of C_2-C_5 alkanes over the temperature range 400-500°C. A full computer modelling of the oxidation process for alkanes thus requires an understanding of the mechanism of alkene oxidation. This oxidation is more complex than the initial stages of alkane oxidation since radical addition to the alkene may occur as well as hydrogen abstraction by the radical. It is not surprising, therefore, that very few rate constants are available for the elementary processes involved. A number of different approaches will be required if the elementary reaction steps are to be disentangled. One such approach involves the addition of small amounts of alkenes to slowly reacting mixtures of $H_2 + O_2$. As with alkane addition, two types of measurement can be made. Study of the loss of hydrocarbon at very low concentrations of additive provides information on radical attack of the alkene, whereas examination of the reaction products (for which a higher concentration of alkene is necessary to provide reasonable yields of products) gives information on the reactions of the radical produced by the primary attack.

(a) Addition of ethene

Results on the addition of C_2H_4 to slowly reacting mixtures of $H_2 + O_2 + N_2$ at $500^\circ C$ have been re-examined. Two types of measurement have been made.

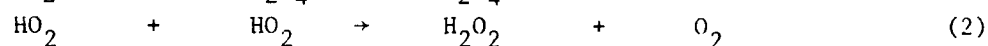
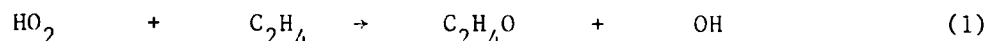
(1) The pressure change ΔP_{50} corresponding to 50% loss of C_2H_4 . Although small corrections are necessary for removal of C_2H_4 by reaction with O atoms, and by reaction with HO_2 in a H-abstraction reaction, the predominant reactions removing C_2H_4 are H and OH abstraction, and H, OH and HO_2 addition. The variation of ΔP_{50} with mixture composition over a wide range provides information on these reactions, though additional information is required if rate constants for all five reactions are to be evaluated.

(2) The yield of products in the early stages of reaction using three mixtures of considerably different $[H_2]/[O_2]$ ratios as indicated below.

Mixture	H_2	O_2	N_2	C_2H_4
	Torr			
I	140	70	285	5
II	140	355	0	5
III	425	70	0	5

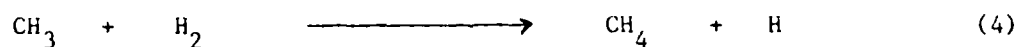
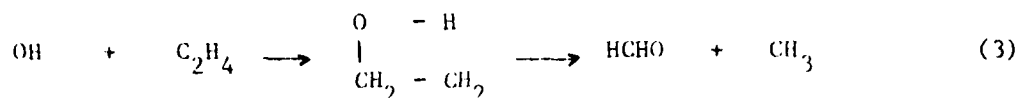
The main initial products, and their suggested mode of formation, are indicated below.

(i) Ethylene oxide (C_2H_4O) is formed almost entirely by addition of HO_2 radicals to C_2H_4 .



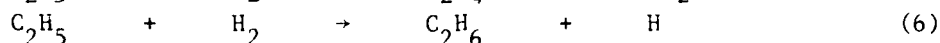
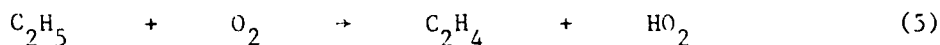
With the rate constants for H and OH addition adjusted to give the best interpretation of the variation of ΔP_{50} , the yields of C_2H_4O (32-40%) require the ratio $k_1/k_2^{1/2} = 1.13 \text{ (dm}^3 \text{ mol}^{-1} \text{ s}^{-1})^{1/2}$. With $k_2 = 2.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_1 = 5.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at $500^\circ C$. This value is in good agreement with that of $6.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, obtained from measurement of the C_2H_4O yields when C_2H_4 is added to mixtures of tetramethylbutane + O_2 in KCl-coated vessels at $500^\circ C$ and 500 Torr total pressure (section 5f).

(ii) Methane. In the $H_2 + O_2$ system, methane appears to be formed early in the reaction and reactions (3) and (4) have been suggested as the most likely source.

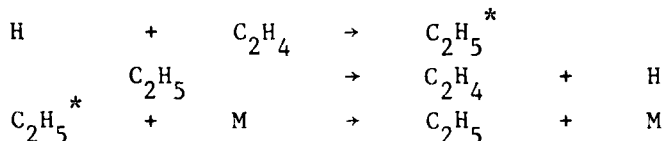


However, when C_2H_4 is added to the tetramethylbutane + O_2 system, where products may be examined in the very early stages of reaction, methane is formed only in trace amounts even under conditions where (3) and (4) should be important. Recent studies have shown that methane is a major product (30-50%) when $\text{C}_2\text{H}_4\text{O}$ is added to slowly reacting mixtures of $\text{H}_2 + \text{O}_2$, and it now seems likely that virtually all the methane with C_2H_4 as additive is formed as a secondary product from $\text{C}_2\text{H}_4\text{O}$. Further work is in progress to confirm this view and to determine the importance of reaction (3).

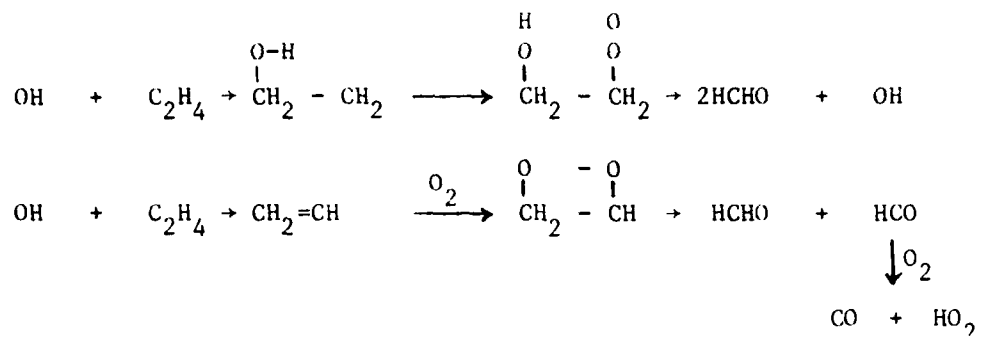
(iii) Ethane is formed by H-addition to C_2H_4 , to give C_2H_5 . The predominant reaction of C_2H_5 will be to reform C_2H_4 by reaction (5), so that no net consumption of C_2H_4 occurs, but a competing reaction (6) is also possible.



The ratio of the rates of reactions (5) and (6) is $k_5[\text{O}_2]/k_6[\text{H}_2]$, so that the yield of C_2H_6 should vary markedly with $[\text{H}_2]/[\text{O}_2]$. This is confirmed experimentally, the initial yields varying from 16% for mixture III to 0.5% for mixture II. From these yields and the known value of k_5/k_6 , obtained from earlier studies of the oxidation of $\text{C}_2\text{H}_5\text{CHO}$ in the presence of H_2 , the value of the rate constant for addition of H atoms to ethylene can be obtained. Allowance is necessary for the fact that, as indicated by previous studies, this addition proceeds through the reaction sequence given below.



(iv) Formaldehyde and Carbon Monoxide. CH_4 , C_2H_6 and $\text{C}_2\text{H}_4\text{O}$ account for about 55% of the products for mixture I, 40% for mixture II, and 70% for mixture III. The only other primary products are CO and HCHO, and although a very small amount of HCHO may be formed in reaction (3), and from the accompanying CH_3 radical, other major sources are required. It is probable that the sequential addition of OH and O_2 , followed by homolysis, provides the major route to HCHO and that CO is formed via the vinyl radical.

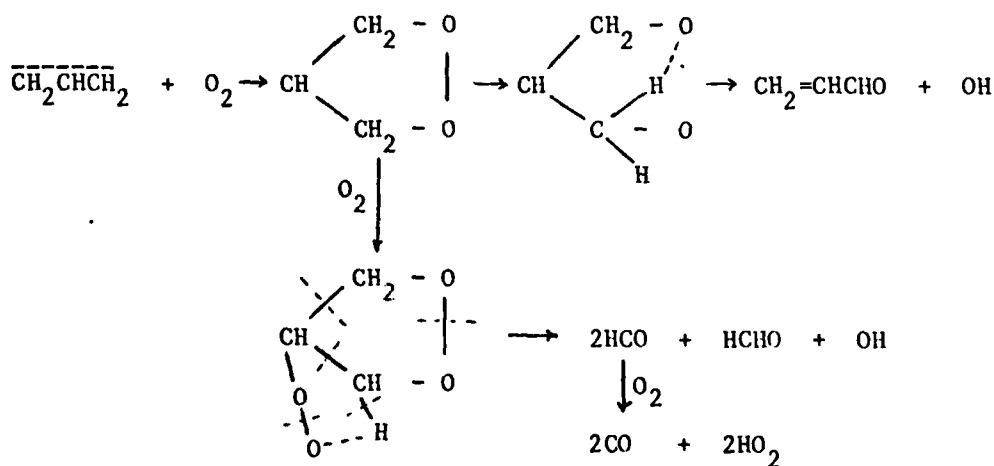


Computer treatment of the results obtained with C_2H_4 is in progress to allow a more detailed interpretation and to evaluate rate constants for the reactions involved. In an attempt to reduce the number of unknown rate constants, a separate study has been made of the reaction of HO_2 radicals with C_2H_4 , using the $\text{TMB} + \text{O}_2$ system as a source of these radicals (section 5f). In addition, studies of the decomposition of $\text{C}_2\text{H}_4\text{O}$ and of its addition to the $\text{H}_2 + \text{O}_2$ reaction show that $\text{C}_2\text{H}_4\text{O}$ is a relatively reactive intermediate in the oxidation of C_2H_4 , playing a major role even in the early stages of reaction.

(b) Addition of propene

From kinetic studies with propene there is no doubt that the rate constants for abstraction by H and OH (to form the resonance-stabilised allyl radical) are at least a factor of 10 lower than expected on energetic grounds by comparison with those for abstraction from alkanes. This marked fall in the rate constants almost certainly arises mainly from low pre-exponential A factors. Strong kinetic and thermodynamic evidence supports this view. For example, the delocalisation of the pi bond in the transition state of the allyl radical reduces the value of ΔS^\ddagger for H abstraction from propene by about $20 \text{ J K}^{-1} \text{ mol}^{-1}$ compared with that for H + propane. Application of transition state theory then gives an A factor for abstraction from propene about one-tenth of that for abstraction from propane.

Results obtained by the addition of propene have been re-examined by computer modelling. The formation of the major initial products, propylene oxide, acetaldehyde, methane, and ethene may be explained by radical addition reactions similar to those discussed in section 3(a) for ethene addition. The products likely to arise from H abstraction (allylic position) from propene, namely acrolein, formaldehyde, and CO represent only about 15-25%, depending on mixture composition, of the propene consumed. A Diels-Alder type of O_2 addition to the allyl radicals is suggested for the formation of these products.



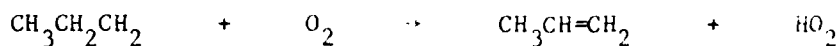
There is little doubt concerning the validity of the mechanism suggested for the formation of the majority of products. However, more precise information concerning the products in the initial stages of reaction at different propene concentrations is essential for the accurate determination of rate constants of the elementary steps. Such information was difficult to

obtain earlier because of rapid consumption of propene. Solenoid-operated taps have now been incorporated into the apparatus to permit precise sampling at times well below 10 seconds, and this together with the more sensitive gas chromatography equipment now available should allow the gathering of the necessary information. Studies of the addition of propene to the tetramethylbutane + O₂ system have also been carried out to facilitate detailed interpretation of the results.

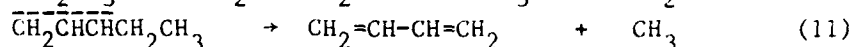
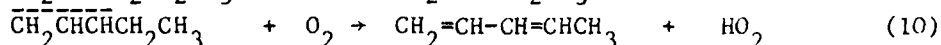
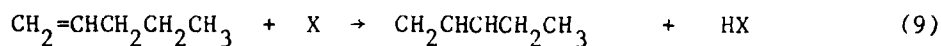
(c) Addition of pentene-1 and pentene-2

Results obtained on the addition of pentene-1 and pentene-2 to slowly reacting mixtures of $H_2 + O_2 + N_2$ at $480^\circ C$ are being interpreted. The initial products can be conveniently divided into four groups according to their mechanism of formation.

(i) By H-abstraction. One difficulty in assessing the relative importance of these reactions relative to radical-addition reactions is the problem of identifying the products resulting from H-abstraction. For alkyl radicals, a reaction of major importance is the formation of a conjugate alkene by a reaction with O_2 involving H atom abstraction from a carbon atom adjacent to the free valency, as for $n-C_3H_7$ radicals below.



However, when such abstraction would have to occur from a doubly bound carbon atom, no evidence has been found for the corresponding reaction with alkenyl radicals. Thus no trace of pentadiene-1,2 or pentadiene-2,3 is obtained from pentene-1 or pentene-2. With pentene-1, the resonance-stabilised radical $\overline{CH_2CHCHCH_2CH_3}$ will be formed predominantly by H-abstraction, and the most probable reactions of this radical are either to react with O_2 to give pentadiene-1,3 (yield 15%) or to decompose to give butadiene-1,3 (yield 12%).



This mechanism would give the ratio $[pentadiene-1,3]/[butadiene-1,3] = k_{10}[O_2]/k_{11}$. The ratio does increase from 1.25 to 5.5 as the pressure of O_2 is increased from 70 Torr (mixture I) to 355 Torr (mixture II). This increase in the ratio is not exactly proportional to $[O_2]$ since some pentadiene-1,3 is formed from the radical $CH_2=CH-CH_2CH_2CH_2$ which reacts uniquely with O_2 to give about 20% of the total pentadiene-1,3. From a reasonable estimate of k_{11} , k_{10} is obtained as $2.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at $480^\circ C$. This is the first value of a rate constant for the formation of a conjugated diene by reaction of an alkenyl radical with O_2 , and, as Table 6 shows, it is considerably below the values for the analogous reaction of alkyl radicals. However, the alkenes are formed in reactions that are 24 to 48 kJ mol^{-1} more exothermic than reaction (10), and there is

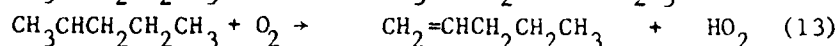
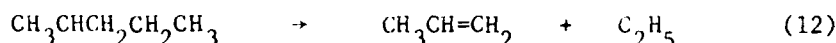
a clear trend in Table 6 for the rate constant to increase with increase in exothermicity. A plot of $\log_{10} k$ against ΔH (kJ mol^{-1}) indicates that expression (i) predicts the values of the rate constant k at 480°C to better than a factor of 1.4.

$$\log_{10} k = 5.50 - 0.0411\Delta H \quad (i)$$

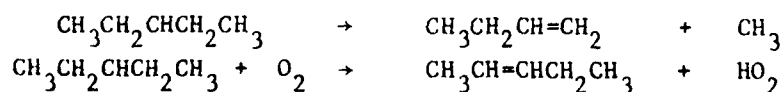
The values of ΔH for the formation of the non-conjugated pentadiene with adjacent double bonds is about 55 kJ mol^{-1} , and use of equation (i) gives an estimated rate constant of about $2 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 480°C , which is a factor of 10^3 lower than k_{10} . The absence of pentadiene-1,2 and pentadiene-2,3 in pentene addition is thus to be expected.

(ii) By H-addition

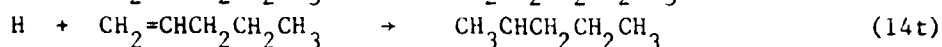
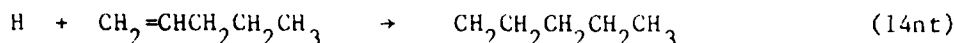
2,4-dimethyloxetan, 2-methyltetrahydrofuran, tetrahydropyran, pentene-2 (from pentene-1) and pentene-1 and trans-pentene-2 (from cis-pentene-2) almost certainly arise solely from pentyl radicals formed by H-addition to the pentenes, and the detailed mechanism has been given in a paper recently published.¹⁵ With propene, the results suggest that nearly all the $n\text{-C}_3\text{H}_7$ radicals, formed in a vibrationally excited state by the exothermic addition (ca. 150 kJ mol^{-1}) of H atoms to propene, decompose to C_2H_4 and CH_3 . With the butenes, the results suggest that a significant fraction (30-50%) of the excited butyl radicals is stabilised, and then reacts. On addition of cis-pentene-2, the products propene and pentene-1 are only formed from the 2-pentyl radical, by decomposition and by reaction with O_2 , respectively.



The initial value of the ratio $[\text{propene}]/[\text{pentene-1}]$ is 4.0, compared with the calculated value of 3.1 using the rate constants k_{12} , k_{13} , obtained for the 2-pentyl radical produced by H-abstraction from pentane (Mixture I). Similarly, the ratio $[\text{trans-pentene-2}]/[\text{butene-1}]$ formed from the 3-pentyl radicals is 3.0 when the radical is produced by H-addition to cis-pentene-2, compared to 2.5 when produced from pentane. There is thus little evidence for an enhanced rate of decomposition of the pentyl radicals formed from the pentene by H addition.



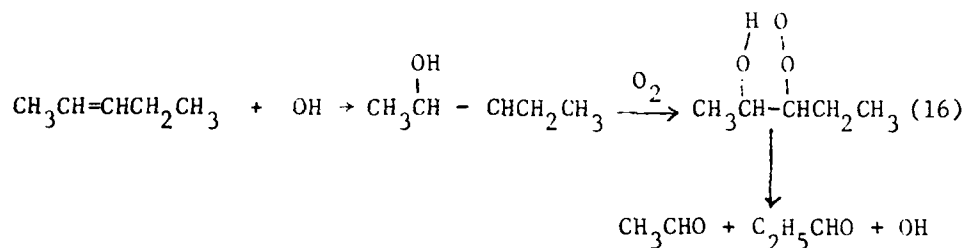
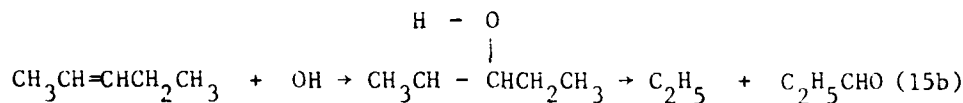
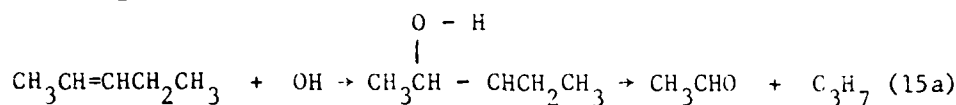
Examination of the yields of products for pentene-1 addition indicates that the ratio of non-terminal to terminal H-addition, $k_{14nt}/k_{14t} = 0.65 \pm 0.2$.



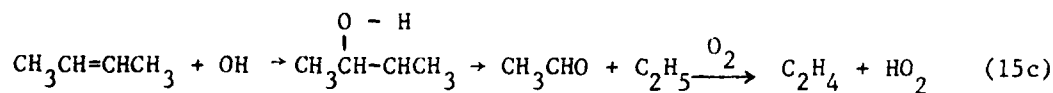
This is much higher than the ratio 0.06 found for C_3H_6 at 298 K and, taken with other evidence, suggests that the discrimination in favour of terminal addition is much reduced as the temperature increases to 500°C.

(iii) By OH addition

The significant yields of CH_3CHO (10%) and C_2H_5CHO (7%) obtained from pentene-2 almost certainly result from OH addition, either by the single step (15a) or (15b) or by the Waddington mechanism involving the addition of O_2 to the initial adduct as in reaction (16).



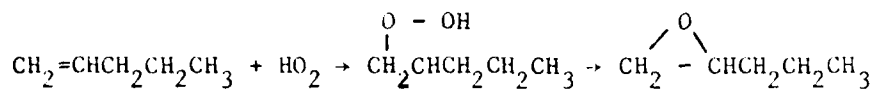
In the case of butene-2, the corresponding reaction (15c) would produce C_2H_4 , which is not detected as a primary product



However, careful analysis of the products suggests that in the case of pentene-2 both mechanisms may be occurring. Further work is thus necessary to establish the relative importance of these two mechanisms.

(iv) By HO₂ addition

The significant yields of 2-propyloxiran (19%) from pentene-1 undoubtedly arise from HO₂ addition, though small amounts will be formed from 1-pentyl and 2-pentyl radicals formed by H-addition to the alkenes.

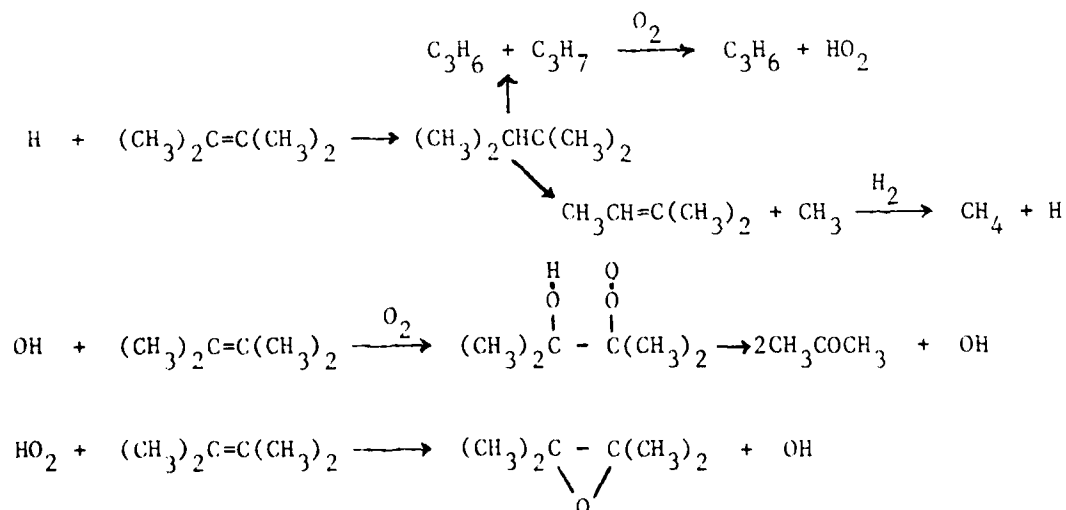


With pentene-2, most of the 2-methyl-3-ethyloxiran appears to come from pentyl radicals, and very little by HO₂ addition. It is planned to measure these rate constants directly by addition of alkenes to the tetramethylbutane + O₂ system discussed later.

Details of the pentene work have now been published.¹⁵

(d) Addition of 2,3-dimethylbutene-2

An investigation has started on the addition of 2,3-dimethylbutene-2 to H₂ + O₂ mixtures at 480°C. Methane, propene, acetone, 3-methylbutene-2, and tetramethyloxiran appear to be the major initial products, which is consistent with earlier work which suggests that addition of H, OH, and HO₂ radicals to the double bond provides the most important route for the oxidation of the alkene.



4. The oxidation of aldehydes

(a) The oxidation of propionaldehyde

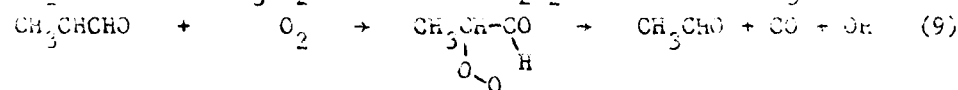
The oxidation of propionaldehyde at 440°C in aged boric-acid-coated vessels¹⁶ has been re-examined with a view to establishing the mechanism of formation of two important products, carbon dioxide and acetaldehyde, which are formed¹⁶ in 5-15% yield, depending on mixture composition.

The main products, ethylene, carbon monoxide and hydrogen peroxide are accounted for by the basic mechanism given below.



The autocatalysis observed in the reaction is attributed¹⁶ to the decomposition of hydrogen peroxide by reaction (6), followed by reaction (7) of the OH radical.

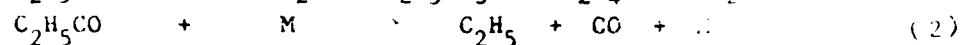
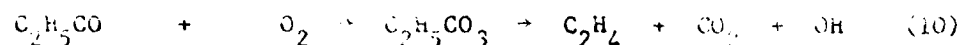
Only a trace of acetaldehyde is formed from C_2H_5 radicals produced by addition of ethane to slowly reacting $H_2 + O_2$ mixtures, so that the reaction $C_2H_5 + O_2 \rightarrow CH_3CHO + OH$, often used in mechanisms of hydrocarbon oxidation, is not the cause of acetaldehyde formation. It is almost certain that acetaldehyde is formed by radical attack at the secondary CH_2 position, followed by reaction of the radical with O_2 .



This sequence is similar to the peroxyradical isomerisation and decomposition (PRID) mechanism given in section (2b).

The ratio $[CO_2]/[CO]$ in the products increases with increase in O_2 concentration, and decreases with increasing addition of inert gas, consistent with a competition between reactions (10) and (2), which gives expression (i) below.

$$d[CO_2]/d[CO] = k_{10}[O_2]/k_2[M] \quad (i)$$



Detailed studies of the variation of $[CO_2]/[CO]$ ratio were made over a wide range of mixture composition, since the system appeared to offer a method of studying the interesting problem of the relative efficiency of

different molecules in reaction (2). However, the ratio $[CO_2]/[CO]$ was found to decrease sharply in the early stages of reaction, to an approximately constant value, and then to rise slowly after about 50% consumption of propionaldehyde. This decrease in the ratio was attributed to the simultaneous occurrence of a surface process forming carbon dioxide, which becomes less important as the chain reaction accelerates. The rise in the later stages of reaction is attributed to the oxidation of carbon monoxide by the radicals OH and HO_2 , and computer treatment confirms the importance of these reactions in the later stages. Confirmation of the existence of a surface formation of carbon dioxide is provided by the increased $[CO_2]/[CO]$ ratio in smaller diameter vessels, whereas the rate of formation of carbon monoxide is unaffected.

A detailed interpretation of the results for a wide range of mixture composition gives the rate constants at $440^\circ C$ listed in Table 11.

Table 11
Rate Constants at $440^\circ C$ in Propionaldehyde Oxidation

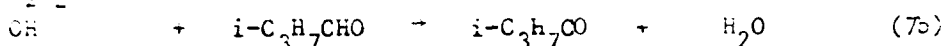
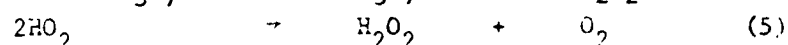
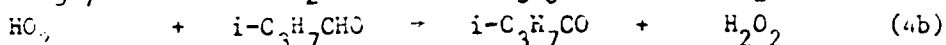
$$\begin{aligned} k_1 &= 0.077 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\ k_4 &= 1.59 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\ k_8 &= 1.1 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\ k_{10}/k_2 &= 0.108 \text{ (M = N}_2\text{)} \end{aligned}$$

The value of k_4 is significantly higher, by a factor of about 4, than preliminary estimates for the rate constant of HO_2 with the secondary CH_2 group in propane, and this suggests that the secondary CH bond is weaker in propionaldehyde than in propane by about 8 kJ mol^{-1} because of the adjacent aldehydic group.

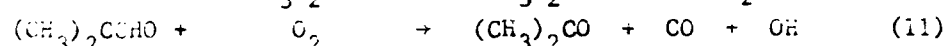
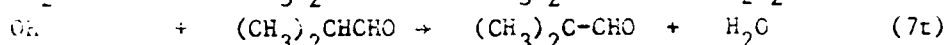
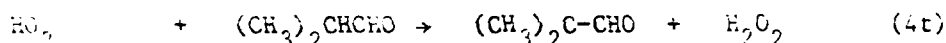
This work has been published.¹⁷

(b) The oxidation of isobutyraldehyde at 440°C

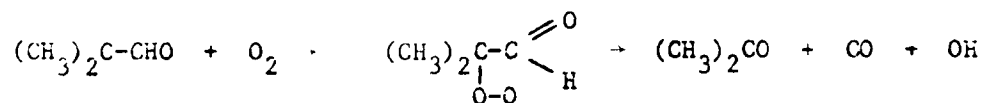
The major products are propene, carbon monoxide and hydrogen peroxide, although small amounts of carbon dioxide (4%), propene oxide (1%), and acetone (in yields of 6-12% depending on mixture composition) are also found. The following scheme accounts for the main reaction products.



The formation of acetone is attributed to reactions (4t), (7t) and (11) below. The increase in the percentage yield of acetone as the reaction proceeds may be used to obtain both k_{4t} and k_{7t} , since the rise in acetone yield is due to the increase in the concentration of the less selective OH radical, as a result of an increasing contribution from the dissociation of the product hydrogen peroxide (reaction 6). The increase in acetone concentration with increasing O_2 concentration is attributed to competition between reactions (11) and (12).

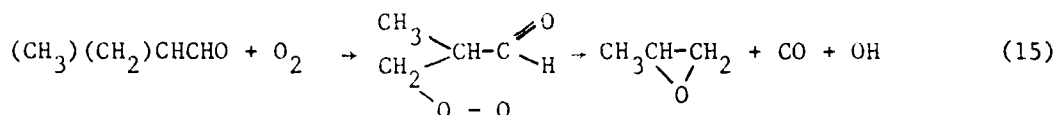
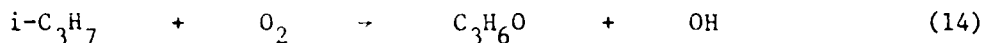


Although the formation of acetone can be represented kinetically by reaction (11), it is undoubtedly formed by a peroxyradical isomerisation and decomposition (PRID) mechanism analogous to that responsible for the formation of acetaldehyde from propionaldehyde.



The full mechanism has been treated by a computer program using a Kutta-Runge integration process to examine the variation of the extent of reaction with time, which gives the rate constants $k_{1b} = 0.12 \pm 0.01 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_{4b} = (1.8 \pm 0.1) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 440°C. From the yields of acetone, the values $k_{4t} = (1.4 \pm 0.1) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_{7t}/k_{7b} = 0.7 \pm 0.1$, $k_{12}/k_{11} = 0.014 \pm 0.002$ ($M = N_2$) have been obtained. The value of k_{4t} is significantly higher than an upper limit of 4×10^4 found for HO_2 attack at the tertiary C-H bond in butane. This confirms the suggestion made in section (1a) that C-H bonds adjacent to an aldehydic group are noticeably weaker than the corresponding bond in an alkane.

Propene oxide is formed both from $i\text{-C}_3\text{H}_7$ radicals by reaction (14) and from the radicals formed by OH and HO_2 attack at the primary CH bonds.



Allowance for the relatively small amount of propene oxide formed by reaction (15) is included in the computer treatment, which gives the best value of k_{14}/k_{3b} as 0.007. This is consistent with a value for 0.010 for the corresponding ratio for $t\text{-C}_4\text{H}_9$ radicals.

As found with propionaldehyde, the $[\text{CO}_2]/[\text{CO}]$ ratio falls sharply as the reaction proceeds, and then rises later due to secondary formation of carbon dioxide from carbon monoxide. This fall has been interpreted in terms of a heterogeneous formation of carbon dioxide in parallel with a homogeneous formation by isomerisation and decomposition of the $(\text{CH}_3)_2\text{CHCO}_3$ radical. However, the yield of carbon dioxide is much lower than in the case of propionaldehyde, and varies rather erratically, so that a detailed study of the mechanism of formation is not considered worthwhile.

This work has been published.¹⁸

(c) Summary of rate constants

Rate constants for the initiation reaction (1) and for the reaction (4) of HO_2 radicals with aldehydes are summarised below.

Table 12
Rate Constants in Aldehyde Oxidation

Aldehyde	k_1 $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	Position of HO_2 attack	k_4 $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	Temp. $^{\circ}\text{C}$
HCHO	0.022	aldehydic	$(5.6 \pm 0.5) \times 10^5$	440
$\text{C}_2\text{H}_5\text{CHO}$	0.081	aldehydic	$(1.52 \pm 0.15) \times 10^6$	440
		secondary CH_2	$(1.5 \pm 0.2) \times 10^5$	440
$n\text{-C}_3\text{H}_7\text{CHO}$		total	$(2.4 \pm 0.5) \times 10^6$	450
$i\text{-C}_3\text{H}_7\text{CHO}$	0.120	aldehydic	$(1.83 \pm 0.1) \times 10^6$	440
		tertiary	$(1.4 \pm 0.2) \times 10^5$	440

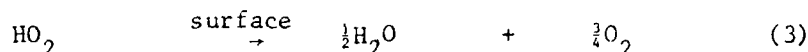
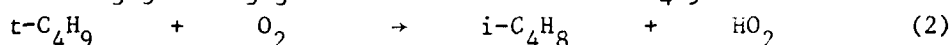
As formaldehyde has two aldehydic C-H bonds, the much lower values both for k_1 and k_4 imply that the activation energy is $8\text{-}12 \text{ kJ mol}^{-1}$ higher for reactions of HO_2 and of O_2 with formaldehyde compared with higher aldehydes, and a similar difference probably applies to the aldehyde C-H bond dissociation energies.

A paper¹⁹ summarising these results and other rate constants for reactions of HO_2 radicals was presented at the Seventeenth International Combustion Symposium at Leeds in August 1978.

5. The oxidation of 2,2,3,3-tetramethylbutane

(a) The oxidation in KCl-coated vessels

Because of the considerable strain caused by the six CH_3 groups around the central C-C bond, the decomposition of 2,2,3,3-tetramethylbutane (TMB) occurs at temperatures 100-150°C lower than needed for straight chain alkanes. The thermolysis of a hydrocarbon is normally a chain reaction, sensitive to surface effects, but these difficulties can be avoided in the case of TMB by carrying out the decomposition in the presence of O_2 . Previous studies have shown that 99% of $\text{t-C}_4\text{H}_9$ radicals react with O_2 to form isobutene according to reaction (2). If the reaction is carried out in a KCl-coated vessel, known to be effective for the destruction of HO_2 radicals, the basic mechanism thus involves reactions (1)-(3).



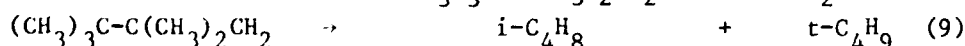
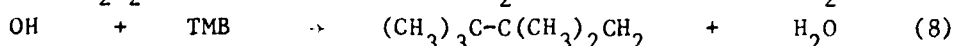
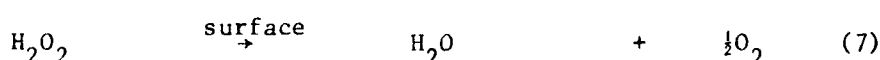
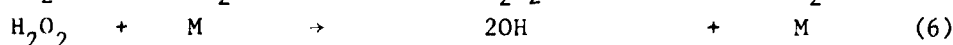
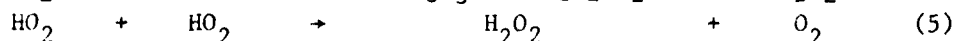
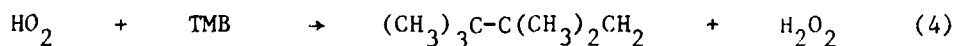
This mechanism gives the stoichiometric equation (s) and the relationships (i) and (ii), which have been confirmed experimentally.



$$\Delta P = 1.5\Delta[\text{TMB}] = 0.75[\text{i-C}_4\text{H}_8] \quad (\text{i})$$

$$-d[\text{TMB}]/dt = k_1[\text{TMB}]^1[\text{O}_2]^0 \quad (\text{ii})$$

However, the experimental rate constant k_{obs} , based on expression (ii), increases slightly (ca.10-20%) with TMB concentration over the range 0.25-4 Torr, and with addition of inert gas. This is attributed to a slight contribution from attack of OH and HO_2 radicals on TMB as the result of the additional reactions (4)-(9) below.



Studies⁹ of the addition of TMB to the $\text{H}_2 + \text{O}_2$ reaction, discussed in section (2) have shown that reaction (9) is the predominant reaction of the TMB radical.

Use of a computer program, based on a stationary state treatment of the radical concentrations and a Runge-Kutta integration of the differential equations for the molecular species, has allowed the evaluation of the rate constants k_1 and $k_4/k_5^{1/2}$ from studies over a range of TMB concentration and total pressure. The chain contribution from reactions (4) and (8) is only about 15% of the total reaction rate and is almost independent of temperature between 420-540°C.

The corrected values of k_{obs} give a good straight line plot of $\log k_1$ against $1/T$ over the range 420-540°C, with Arrhenius parameters $A_1 = 1.2 \times 10^{17} \text{ s}^{-1}$, $E_1 = 295.4 \pm 1.5 \text{ kJ mol}^{-1}$, which may be compared with $A_1 = 2 \times 10^{16} \text{ s}^{-1}$, $E_1 = 286.5 \text{ kJ mol}^{-1}$ over the range 713-868°C, obtained by Tsang²⁰ using a shock tube. Combination of Tsang's data, suitably corrected, with the present data gives $A_1 = 6.0 \times 10^{16} \text{ s}^{-1}$, $E_1 = 290.4 \pm 1.5 \text{ kJ mol}^{-1}$ over the range 420-868°C. Combination of the value of E_1 with that for the reverse reaction and with other thermodynamic data gives the enthalpy of formation $\Delta_f H_{298}^0 = 44.0 \pm 4.0 \text{ kJ mol}^{-1}$ for the $t\text{-C}_4\text{H}_9$ radical, which is at least 10 kJ mol^{-1} higher than previously accepted values. The value of $\Delta_f H_{298}^0$ leads to a bond dissociation energy $D_{298}^0(t\text{-Bu} - \text{H})$ of 396.6 kJ mol^{-1} , which again is significantly higher than the previously accepted value of 382 kJ mol^{-1} . Recommended values for the bond dissociation energies in the $\text{C}_1\text{-C}_4$ alkanes are given later.

This work has been published.²¹

(b) The reaction of HO_2 radicals with 2,2,3,3-tetramethylbutane

The increase in the observed value of the rate constant k_{obs} , obtained from expression (i), with increase in TMB concentration and on addition of inert gas is due to a small chain contribution (chain length less than unity) from reactions (4) and (8). At the lower temperatures (420 and 440°C) this is predominantly due to reaction (4), but as the temperature rises the increased dissociation of H_2O_2 causes an increasing contribution from reaction (8); at the same time the contribution from HO_2 attack decreases because the second-order reaction (5) becomes increasingly dominant as the concentration of radicals increases. Computer interpretation of the mechanism involving reactions (1)-(9) gives a preliminary value of $k_4 = 1.7 \times 10^4$ at 440°C. This value for k_4 represented the first direct determination of a rate constant for the reaction of HO_2 radicals with an alkane, and was reported¹⁹ at the Seventeenth International Combustion Symposium at Leeds in 1978.

However, although the individual values of the surface termination constant k_3 and the homogeneous termination constant k_5 are known, the total termination rate is not the sum of the two individual termination rates because of interaction between the homogeneous termination, which gives a uniform concentration of radicals across the reaction vessel, and the surface destruction, which gives a diffusion-controlled profile. The occurrence of homogeneous termination increases the concentration gradient near the vessel surface, so that the rate of surface termination is greater than when homogeneous termination is absent. There has been only one study of the extent of this interaction, which does not provide results in a convenient form for the present problems. Calculations with linear homogeneous termination, where the differential equations can be integrated algebraically, show that the total termination rate may be increased by as much as 20%. Since this means that the concentration of HO_2 radicals may be about 20% below that calculated using conventional treatments, appreciation of this interaction is essential if accurate rate constants are to be obtained using the oxidation of TMB in KCl-coated vessels as a source of HO_2 radicals.

With mutual termination, there is no explicit solution of the simultaneous differential equations involved and numerical methods have to be adopted. In collaboration with Dr. Howarth of the Department of Applied Mathematics, a suitable program has been written to solve the second-order

differential equations in the case where the chain initiation results only from the decomposition of TMB. Since the concentration of TMB is uniform across the vessel, the rate of initiation is also uniform. A Runge-Kutta type procedure was employed with Merson's modification used as a basis of an automatic step-size adjustment throughout the procedure in order to obtain uniform accuracy.

The treatment involved the dimensionless parameters $X = x/r$, $N = Dn/r^2\theta$, and $A = \delta r^4\theta/D^2$,

where x is the distance from the vessel centre (cylindrical),
 r is the vessel radius,
 D is the diffusion coefficient,
 n is the chain centre concentration,
 θ is the initiation rate,
 δ is the mutual termination constant.

To avoid the singularity at the centre of the vessel ($X = 0$), a power series in X was developed and used to enable integration to commence a small distance away from the singularity. Care was taken to ensure adequate convergence. An iteration scheme was employed to find the correct value of the centre concentration N at $X = 0$. It was found that as the value of A increased, increasing accuracy in selecting the initial value of N ($X = 0$) was required if the iteration scheme was to succeed. The results show that again the total termination rate is some 20% higher than if interaction is ignored.

However, the real situation is more complex since H_2O_2 can dissociate by reaction (6) and thus also produce chain centres. Moreover, since H_2O_2 is produced from HO_2 , its concentration is not uniform across the vessel, and its diffusion to the surface has also to be considered. This creates a pair of simultaneous differential equations which have to be numerically integrated and, to obtain a solution, starting values of the concentrations of HO_2 and H_2O_2 at the centre of the vessel have to be provided. If the guesses are not sufficiently accurate, the program finds erroneous solutions. With the high values of A involved under many experimental conditions, the accuracy needed in the guessed concentrations of HO_2 and H_2O_2 at $X = 0$ made solution extremely difficult. An alternative method, involving the use of the finite difference method, was therefore devised. This proved much easier to operate than the Runge-Kutta method and comparisons showed that it gave effectively identical results. The corrections to $[HO_2]$ varied from 0 to -20%, to $[HO_2]^2$ from -25% to +24%, and

to $[H_2O_2]$ from -15% to +15%.

These corrections were introduced into the computer program described in section 5(a), and the optimum values of k_1 and $k_4/k_5^{1/2}$ redetermined. The values of k_1 (given in section 5(g)) are effectively unaltered but $k_4/k_5^{1/2}$ is increased about 20% at 440°C, entirely because of the interaction phenomena. On the assumption that $k_5 = 2 \times 10^9$ litre mol⁻¹ s⁻¹, independent of temperature, the values of k_4 at various temperatures are summarised below.

Table 13

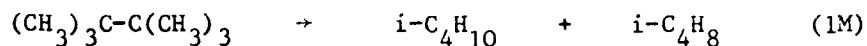
Temp. °C	Number of mixtures	Range of TMB/Torr	Range of pressure/Torr	$k_4/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$	Data
418	8	0.25-4.0	60-500	1.15×10^4	Keen ²²
437.5	9	0.25-4.0	60-500	2.04×10^4	Keen ²²
440	7	0.50-4.0	60-500	1.95×10^4	Evans ²¹
466	10	0.25-4.0	60-500	3.01×10^4	Keen ²²

These results are discussed further in section 5(g). A paper giving a general discussion of problems of chain reactions with surface termination has been published.²³

With accurate values of k_4 available, the TMB oxidation can now be used as a source of HO_2 radicals so as to obtain rate constants for HO_2 radicals + some additive, as described in section 5(f).

(c) The molecular decomposition of 2,2,3,3-tetramethylbutane

A small amount (ca. 1%) of i-butane is found in the decomposition of TMB in the presence of O_2 . The rate of production of i-butane is first order in TMB, and is independent of the concentration of O_2 , of inert gas addition, and of vessel diameter. These observations leave as the only possibility a molecular mechanism for i-butane formation.

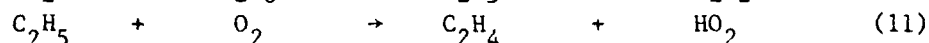
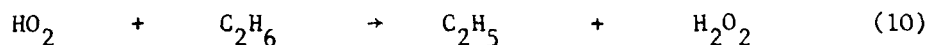


Study of the molecular decompositions between 420-540°C gives the Arrhenius parameters $A_{1M} = 7.8 \times 10^{13} \text{ s}^{-1}$, $E_{1M} = 275 \pm 1.5 \text{ kJ mol}^{-1}$.

The A factor is consistent with that expected for a four-centre transition state. These parameters appear to be the first reported for the non-chain, molecular decomposition of an alkane. This work has been published.²⁴

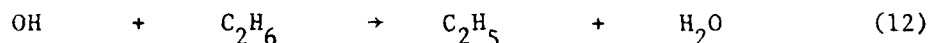
(d) Reaction of C_2H_5 radicals with O_2

In a previous report, the rate constant for reactions of HO_2 radicals with C_2H_6 was determined by measuring the relative yields of isobutene and C_2H_4 formed when C_2H_6 is added to TMB + O_2 mixtures. With the simplest mechanism involving reactions (1)-(3), (10) and (11), the relative yields are given by equation (iii)

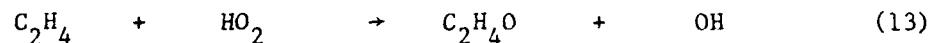


$$d[C_2H_4]/d[i-C_4H_8] \rightarrow k_{10}[C_2H_6]/k_3 \quad (iii)$$

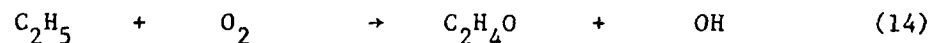
In an accurate evaluation of k_{10} , allowance must be made for the occurrence of reactions (4)-(9), as well as reaction (12), and detailed computer interpretation is in progress.



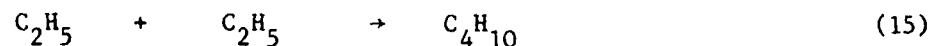
Although the predominant product formed from C_2H_6 is C_2H_4 , a trace of ethylene oxide (C_2H_4O) is formed and the ratio $[C_2H_4]/[C_2H_4O]$ can be accurately measured as a result of the increased sensitivity and reproducibility possible with a recently acquired Perkin-Elmer Sigma I gas chromatograph. It is found that at small extents of reaction, the ratio $[C_2H_4]/[C_2H_4O]$ is constant at 95 at $500^\circ C$, but that the ratio decreases as the reaction proceeds, almost certainly because of reaction (13).



Since the initial ratio $[C_2H_4]/[C_2H_4O] = k_{11}/k_{14}$, the variation of the initial ratio with temperature over the range $400-540^\circ C$ has been used to obtain the Arrhenius parameter $A_{11}/A_{14} = 13.6 \pm 2.1$, $E_{14} - E_{11} = 12.5 \pm 1.0$ kJ mol⁻¹.



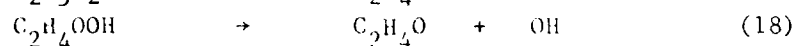
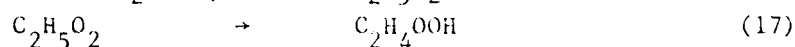
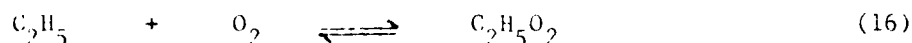
From measurements of the trace amounts of butane formed by reaction (15), the concentration of C_2H_5 radicals can be calculated from the known value of k_{15} .



Since $d[C_2H_4]/dt = k_{11}[C_2H_5][O_2]$, the measurement of the rate of formation

of C_2H_5 can be used to obtain $k_{11} = 7.7 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 540°C . Combination of this value with an independent estimate at 440°C gives $A_{11} = 10^{8.93} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $E_{11} = 16.2 \text{ kJ mol}^{-1}$, which are considered to be the most reliable parameters available for this reaction.

From these parameters for A_{11} , E_{11} , values of $A_{14} = 6.3 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $E_{14} = 28.7 \text{ kJ mol}^{-1}$ are obtained. However, the overall reaction (14) is considered to proceed by a peroxy radical isomerisation and decomposition process, represented by equations (16)-(18).

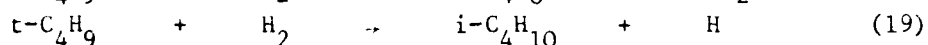
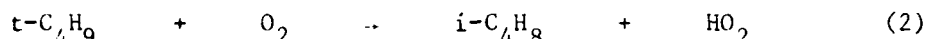


On the assumption that (18) is the sole reaction of C_2H_4OOH radicals, and that reaction (16) is effectively equilibrated, the rate constant $k_{14} = K_{16}k_{17}$. Using Benson's additivity rules to evaluate K_{16} , the experimental values of A_{14} , E_{14} given above lead to $A_{17} = 10^{13.29} \text{ s}^{-1}$, $E_{17} = 144.0 \pm 10 \text{ kJ mole}^{-1}$. The values are the first experimental determinations of the Arrhenius factors for such reactions. This value of A_{17} is a factor of ten higher than the figure suggested by Benson for similar isomerisations of alkylperoxy radicals to the hydroperoxyalkyl radical which give oxetans on decomposition. Since these involve a 6-membered ring in the transition state, compared to a 5-membered ring of reaction (17), this is consistent with transition state theory which indicates that the A factor for such isomerisation reactions should increase significantly as the ring size decreases.

This work has now been published.²⁵

(e) Reactions of t-butyl radicals

The basic mechanism involving reactions (1)-(3) indicates that the decomposition of TMB in the presence of O_2 offers a controlled source of t-butyl radicals. If H_2 is added, i- C_4H_{10} is formed by reaction (19), and the competition between reactions (2) and (19) gives expression (iv).



$$d[i-C_4H_{10}]/d[C_4H_8] = k_{19}[H_2]/k_2[O_2] \quad (iv)$$

In using equation (iv) allowance must be made for the occurrence of reactions (9) and (1M) in which i-butene is formed but not via the $t-C_4H_9$ radical, and for reaction (1M) which forms i-butane by a molecular process. Because of the small yields of i-butane, high ratios (100-300) of $[H_2]/[O_2]$ must be used. The ratio $d[i-C_4H_{10}]/d[i-C_4H_8]$ is found to be proportional to $[H_2]/[O_2]$ as predicted by equation (iv), and the ratio k_2/k_{19} varies from 11,950 to 3,180 over the temperature range 440-540°C, corresponding to values of $A_2/A_{19} = 0.35 \pm 0.10$, $(E_{19} - E_2) = 61.9 \pm 2.0$ kJ mol⁻¹. Use of the known value of k_{19} and of thermochemical data for reaction (19) gives the values $A_{19} = 2.30 \times 10^9$ dm³ mol⁻¹ s⁻¹, $E_{19} = 71.0 \pm 6.0$ kJ mol⁻¹, $A_2 = 8.0 \times 10^8$ dm³ mol⁻¹ s⁻¹, $E_2 = 9.1 \pm 10$ kJ mol⁻¹. Although subject to some uncertainty, the low value for E_2 confirms the view that reactions of alkyl radicals with O_2 to give the conjugate alkene have a low activation energy.

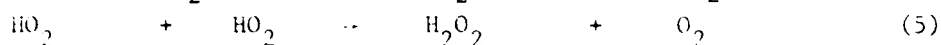
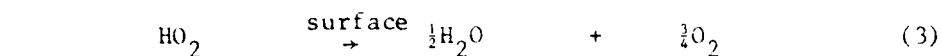
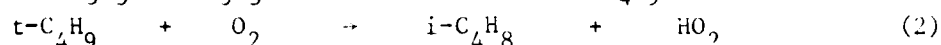
The data are mostly self-consistent with a value of $\Delta_f H(t-C_4H_9) = 16.1$ kJ at 480°C. This corresponds to a value of $D_{298}^0(t-C_4H_9)$ of 392.7 kJ mol⁻¹. This value is some 10 kJ mol⁻¹ higher than earlier estimates by other workers, but is consistent with values recommended for other alkyl radicals which are listed in section 6.

This work has been published.²⁶

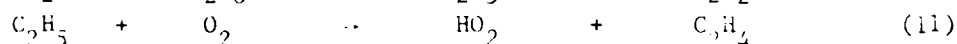
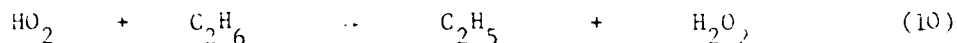
(f) Reactions of HO₂ radicals with alkanes, alkenes and carbon monoxide

Ethane

There is considerable difficulty in finding a suitable source of HO₂ radicals in the temperature range 400-550°C, since with most methods of production of this radical, it is accompanied by more reactive radicals. However, the decomposition of TMB in the presence of O₂ offers a source of HO₂ radicals since, as already indicated, the mechanism is described with reasonable accuracy by reactions (1)-(3) and (5) below.



An added alkane, such as ethane, will be removed by reaction (10), the predominant reaction of the C₂H₅ radicals produced being to form C₂H₄ by reaction (11).



If HO₂ radicals are predominantly destroyed by reaction (3), the above scheme gives the rate expression (v), whereas if reaction (5) predominates over (3), the rate expression (vi) is obtained.

$$d[\text{C}_2\text{H}_4]/d[\text{i-C}_4\text{H}_8] = k_{10}[\text{C}_2\text{H}_6]/k_3 \quad (v)$$

$$d[\text{C}_2\text{H}_4]/d[\text{i-C}_4\text{H}_8] = 0.5k_{10}[\text{C}_2\text{H}_6]/(k_1k_5[\text{TMB}])^{1/2} \quad (vi)$$

Expression (v) is found to be approximately correct at low temperatures and pressures, where the HO₂ concentration is low, whereas expression (vi) is approached as the temperature and pressure increase. For accurate treatment, allowance must be made for the dissociation of hydrogen peroxide, reaction of HO₂ radicals with TMB, reaction of OH radicals both with ethane and TMB, reactions of C₂H₅ and t-C₄H₉ radicals with O₂ to give products other than the conjugate alkene, formation of i-butene by the molecular reaction (1M) and by the decomposition reaction (9) of the TMB radical. All these effects are allowed for in a suitable computer treatment of the mechanism. Allowance is also made for a small amount of ethylene formed by a surface reaction, this process being most important at low TMB concentrations and low ethane concentrations.

Preliminary interpretation has given a value of $k_{10} = 1.27 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, based on $k_5 = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and this value was reported¹⁹ at the Seventeenth International Combustion Symposium at Leeds in 1978. With the development of a procedure, described in section (5b), for allowing for the interaction between homogeneous and heterogeneous termination, more accurate values have been obtained over the temperature range 420 - 520°C, which are summarised below. It is assumed that k_5 is independent of temperature.

Table 14
Rate Constants for $\text{HO}_2 + \text{C}_2\text{H}_6$

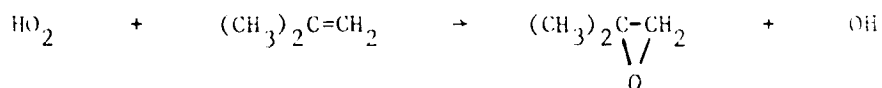
Temperature/°C	420	440	470	500	520
$k_{10}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	8.8×10^3	1.35×10^4	2.9×10^4	5.2×10^4	1.04×10^5

The log k, 1/T plot gives $E_{10} = 98 \text{ kJ mol}^{-1}$, $A_{10} = 2.1 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Both these values seem on the high side, and confirmation of the values of k_{10} , particularly at the higher temperatures, by the use of boric-acid-coated vessels, is planned. Nevertheless, these studies show that the decomposition of TMB in the presence of O_2 provides a very convenient source of HO_2 radicals, and a detailed study of their reactions with a wide range of alkanes and alkenes is planned. Very few rate constants for these reactions are currently available.

Isobutene

Isobutene is the major initial product (99% yield) when TMB is decomposed in the presence of O_2 in KCl-coated vessels over the temperature range 420 - 540°C. Later in the reaction, secondary products are formed from isobutene and affect the overall kinetics. Studies have, therefore, been made of the addition of isobutene to slowly reacting mixtures of $\text{TMB} + \text{O}_2$ with two major objectives.

- (i) A determination of the Arrhenius parameters for the reaction of HO_2 radicals with isobutene.



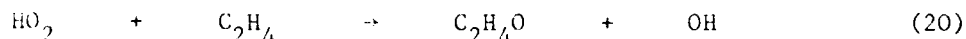
Very little information is available on the addition reactions of HO_2 radicals with alkenes.

(ii) A general study of the chemistry of isobutene oxidation in the TMB + O₂ system, which will also permit the interpretation of the parent system to be carried out further into reaction than is possible at present.

Analytical studies at 470°C, using a mixture containing 2, 1, 30, and 27 Torr of TMB, isobutene, O₂, and N₂, show that the major initial products are acetone (20% yield), isobutene oxide (20%), propene (15%), methane (11%), 2-methylprop-2-en-1-al (11%), isobutyraldehyde (5%), ethylene (5%), 2-methylbutene-1 (5%), and allene (4%). Analyses are currently being carried out for HCHO, CO, and CO₂. Variation in the mixture composition does not greatly affect the product distribution. The concentration of isobutene oxide reaches a maximum early in the reaction since it is rapidly removed by isomerisation processes; this has been confirmed by direct studies of the isomerisation of isobutene oxide. In view of the reactivity of isobutene oxide, further studies with much shorter sampling times are required to distinguish between the primary products formed from isobutene, and secondary products formed from isobutene oxide.

Ethylene

Detailed studies have been made of the addition of C₂H₄ to the TMB + O₂ reaction over the temperature range 400 - 500°C and over the wide pressure range 15 - 500 Torr. If the formation of ethylene oxide is represented by equation (20), then stationary state treatment of the simplest mechanism, involving reactions (1), (2), (3), (5), (8), (9) and (20), gives the relative rate of formation of ethylene oxide and isobutene as expression (vii) if HO₂ is predominantly destroyed at the surface, and as (viii) if HO₂ is removed by the mutual termination reaction (5).



$$\frac{d[\text{C}_2\text{H}_4\text{O}]}{d[\text{i-C}_4\text{H}_8]} = \frac{k_{20}[\text{C}_2\text{H}_4]}{k_3} \quad (\text{vii})$$

$$\frac{d[\text{C}_2\text{H}_4\text{O}]}{d[\text{i-C}_4\text{H}_8]} = \frac{0.5k_{20}[\text{C}_2\text{H}_4]}{(k_1k_5[\text{TMB}])^{1/2}} \quad (\text{viii})$$

The initial experimental value of the ratio $[\text{C}_2\text{H}_4\text{O}]/[\text{i-C}_4\text{H}_8]$ is found to be markedly dependent on pressure. This is to be expected because the surface destruction constant k_3 is inversely dependent on pressure since HO₂ radicals are efficiently destroyed at the surface. Since the relative importance of reactions (3) and (5) varies with TMB concentration, total pressure and temperature, a computer treatment is necessary using a mechanism which incorporates (4), (6) and (7), as well as possible

reactions of OH radicals with C_2H_4 . When the variation of HO_2 concentration with pressure is allowed for in this way, a small residual variation of k_{20} with pressure is found. Three explanations may be suggested.

(a) The overall rate constant k_{20} is the result of the mechanism represented by reactions (21), (-21) and (22), and is given by expression (ix).



$$k_{20} = k_{21}k_{22}[M]/(k_{-21} + k_{22}[M]) \quad (ix)$$

(b) C_2H_4O might be formed by the reaction sequence (23) and (24). Increased dissociation of H_2O_2 by reaction (6) increases the OH concentration as the pressure increases, so that k_{20} , which is determined by the total yield of C_2H_4O formed through both HO_2 and OH, would increase with pressure.



However, in this case, k_{20} would increase as $[C_2H_4]/[TMB]$ increases, since this favours the reaction of OH with C_2H_4 rather than TMB. No such increase is found experimentally, so that this explanation can be eliminated.

(c) The calculation of the variation of HO_2 concentration with pressure is dependent on the value taken for k_3 as well as for the various diffusion constants. It is possible, though unlikely, that uncertainties in these values could cause a spurious variation of k_{20} with pressure. Further work, including studies in boric-acid-coated vessels, is needed to establish the exact pressure dependence of k_{20} .

In addition to C_2H_4O , significant yields of HCHO are also formed on addition of C_2H_4 . CH_4 is also formed, but the curve is autocatalytic and mathematical treatment suggests that the initial rate of formation of CH_4 is effectively zero. This rules out the suggested reaction (25), and indicates that HCHO is formed by reactions (23) and (26).

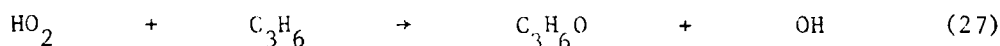


Reaction (25) was originally suggested as a result of the observation that CH_4 was a product in the addition of C_2H_4 to slowly reacting mixtures of $H_2 + O_2$, and the value of complementary studies using the decomposition of TMB as a source of radicals is clearly shown. Further studies to confirm that CH_4 is a secondary product in the $C_2H_4 + H_2 + O_2$ system are in progress.

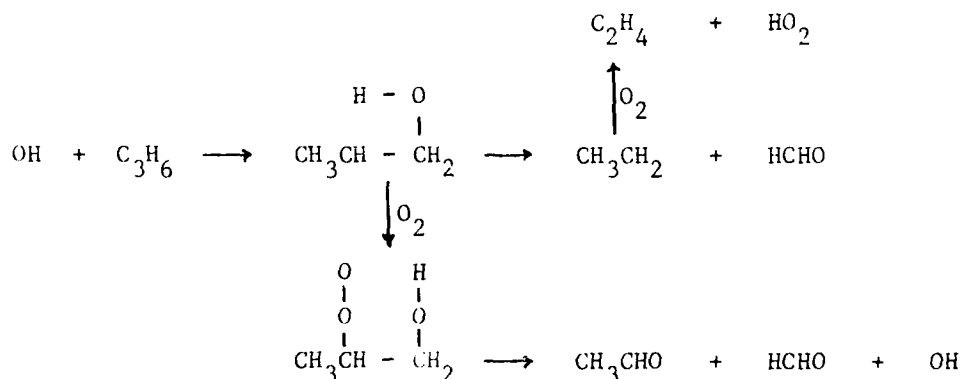
The computer treatment gives the limiting high pressure value of k_{20} at 500°C as $6.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, based on $k_5 = 2 \times 10^9$. From the variation of k_{20} with temperature over the range $400 - 500^{\circ}\text{C}$, $A_{20} = 2.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $E_{20} = 80.9 \pm 5 \text{ kJ mol}^{-1}$. These parameters are the first values obtained for addition of HO_2 to a carbon-carbon double bond.

Propene

Because of the difficulty, discussed above, of the variation of HO_2 concentration with pressure in KCl-coated vessels, studies of the addition of propene have been made in aged boric-acid-coated vessels, following the study of the $\text{TMB} + \text{O}_2$ reaction in such vessels described in section (5g). Measurement of the product yields has been made over the temperature range $400 - 500^{\circ}\text{C}$ at various pressures between 15 and 500 Torr. The major initial products are propene oxide, C_2H_4 , CH_3CHO , HCHO , and CO , with smaller amounts of $\text{CH}_2=\text{CHCHO}$ and CH_4 . Propene oxide is almost certainly formed in the overall reaction (27), although it may be a multistage process similar to reactions (21) and (22) for the formation of $\text{C}_2\text{H}_4\text{O}$ from C_2H_4 .

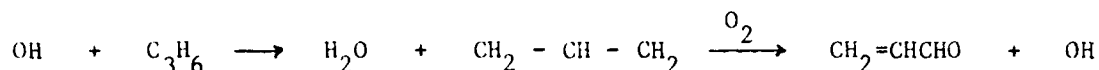


The yields of C_2H_4 and CH_3CHO relative to that of propene oxide increase with time, particularly at the higher temperatures and pressures where the decomposition of H_2O_2 into OH radicals is important, which suggests that these products are formed in OH addition reactions.



As 99% of C_2H_5 radicals react with O_2 to give C_2H_4 , then $[\text{CH}_3\text{CHO}]/[\text{C}_2\text{H}_4]$ should be proportional to $[\text{O}_2]$, as observed experimentally.

The relative yield of $\text{CH}_2=\text{CHCHO}$ also increases with time, and therefore it is likely that $\text{CH}_2=\text{CHCHO}$ is formed from the resonance-stabilised allyl radical, produced by H abstraction from $\text{CH}_3\text{CH}=\text{CH}_2$ mainly by the OH radical.

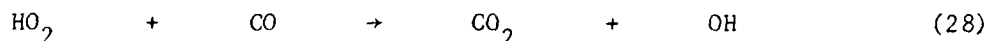


It is likely that CO is also produced from the allyl radical, although the precise nature of the reaction is still in doubt.

The results are currently being interpreted by computer treatment. A preliminary value of $k_{27} = 1.2 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 500°C , similar to the value of $k_{20} = 6.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the formation of $\text{C}_2\text{H}_4\text{O}$ from the addition of HO_2 to C_2H_4 , has been obtained.

Carbon monoxide

Although the reaction between HO_2 radicals and CO is an important step in various combustion processes, its rate constant and Arrhenius parameters are still uncertain.

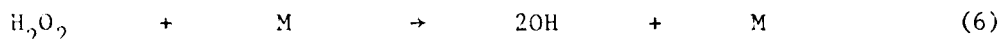


Attempts have been made to study reaction (28) by the addition of CO to mixtures of tetramethylbutane + O_2 in KCl-coated vessels. Although reproducible results can be achieved by careful conditioning of the reaction vessel, it is clear that a significant proportion of the CO_2 is formed at the vessel surface, and thus a reliable rate constant cannot be determined.

Recently, however, aged boric-acid-coated vessels have been used with considerable success and surface effects appear to be absent. Although the radical ratio $[\text{OH}]/[\text{HO}_2]$ is considerably higher than in the KCl-coated vessels, the formation of CO_2 through the reaction of OH radicals with CO may be accurately calculated and does not exceed about 10% of the total yield. A study has been made over the temperature range $420 - 500^\circ\text{C}$. The values obtained for k_{28} are in close agreement with those previously reported, but cover a bigger temperature range, and should enable reliable Arrhenius parameters for this reaction to be determined.

(g) The oxidation of 2,2,3,3-tetramethylbutane in boric-acid-coated vessels

Although the efficient destruction of HO_2 radicals and of H_2O_2 at a KCl-coated surface minimises the role of OH radicals produced by the dissociation reaction (6) of H_2O_2 , use of this surface has two disadvantages.



(i) As the temperature, and hence the concentration of HO_2 , increase, H_2O_2 is formed increasingly by reaction (5) and its dissociation becomes more important. Allowance for this is complicated by the interaction between homogeneous and heterogeneous termination, discussed in section (5b).

(ii) The KCl-coated surface deteriorates with use, so that weekly re-coating is necessary, thus slowing down the experimental work.

As a consequence, the reaction has been re-examined in aged boric-acid-coated vessels, where the surface destruction of HO_2 and H_2O_2 is effectively negligible. A detailed study has been made between 400 and 520°C. Because of the very short reaction times necessary at the higher temperatures, solenoid valves were used, the opening and closing of these valves being controlled by a microprocessor unit. To minimise complications resulting from the formation of the product i-butene, consumption of TMB was restricted to a maximum of 5%. To avoid excessive dissociation of the reaction product H_2O_2 , the main studies were made at a total pressure of 15 Torr, though a range of pressures was studied. A range of TMB concentrations from 0.1 to 4 Torr was used.

In contrast to the behaviour in KCl-coated vessels, the reaction was markedly autocatalytic, the extent increasing as the total pressure was increased by addition of N_2 , due to the increased rate of reaction (6). Since the H_2O_2 concentration does not reach a stationary value, but rises continuously with time for at least 30% reaction, the partial differential equations for reactants and for H_2O_2 have to be solved by numerical integration using a computer treatment.

The only unknown parameters required to operate the computer program are the values of k_1 , of $k_4/k_5^{1/2}$, and of a_{TMB} , the coefficient for the efficiency of TMB in reaction (6) relative to H_2 . The computer program calculates the extent of reaction at various reaction times, and compares the observed and calculated values for a range of mixtures. Incorporation of an optimisation procedure enables the optimum values of k_1 and $k_4/k_5^{1/2}$ giving minimum r.m.s. deviation to be obtained. The value of k_1 was found to be

effectively independent of that taken for a_{TMB} , whereas the value obtained for $k_4/k_5^{\frac{1}{2}}$ decreased significantly as a_{TMB} was varied over the range 1 - 10. Unfortunately the minimum r.m.s. deviation did not vary sufficiently with a_{TMB} for a value to be selected, though values of a_{TMB} above 5 were clearly excluded. The value obtained for $k_4/k_5^{\frac{1}{2}}$ from results in KCl-coated vessels is effectively independent of a_{TMB} , and to obtain values of $k_4/k_5^{\frac{1}{2}}$ in boric-acid-coated vessels in agreement with those obtained in KCl-coated vessels, a value of $a_{\text{TMB}} = 2.5$ was required. The values thus obtained for k_1 and $k_4/k_5^{\frac{1}{2}}$ are summarised in Table 15, which also gives the values obtained for k_1 in KCl-coated vessels from the work described in section (5b).

Table 15
Variation of k_1 and $k_4/k_5^{\frac{1}{2}}$ with temperature

Temp./°C	KCl-coated vessel	Aged boric-acid-coated vessel	
	$k_1/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$k_1/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$(k_4/k_5^{\frac{1}{2}})/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})^{\frac{1}{2}}$
400	-	1.45×10^{-6}	0.24
420	-	6.17×10^{-6}	0.30
440	2.56×10^{-5}	2.77×10^{-5}	0.41
470	2.01×10^{-4}	1.70×10^{-4}	0.84
500	1.33×10^{-3}	1.37×10^{-3}	0.98
520	3.98×10^{-3}	4.05×10^{-3}	2.41
542	1.29×10^{-2}	-	-

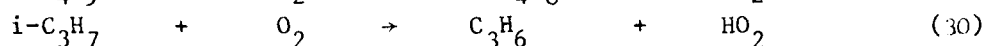
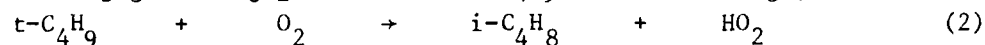
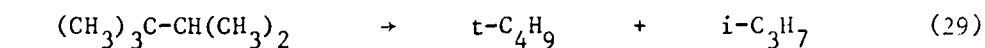
The $\log k_1$, $1/T$ plot gives $A_1 = 1.26 \times 10^{17} \text{ s}^{-1}$, $E = 295.8 \text{ kJ mol}^{-1}$. These values may be compared with $A_1 = 1.08 \times 10^{17}$, $E_1 = 295.1 \text{ kJ mol}^{-1}$, obtained from studies in KCl-coated vessels. Combination of the values in both boric-acid-coated and KCl-coated vessels gives $A_1 = 1.04 \times 10^{17}$, $E_1 = 294.7 \text{ kJ mol}^{-1}$. The differences are within experimental error, and the estimated accuracy in E_1 is within $\pm 3 \text{ kJ mol}^{-1}$. The close agreement with previously published values²¹ of $A_1 = 1.20 \times 10^{17} \text{ s}^{-1}$, $E_1 = 295.4 \text{ kJ mol}^{-1}$ confirms the validity of the thermodynamic data for the t-butyl radical suggested in section (5a).

The plot of $\log (k_4/k_5^{\frac{1}{2}})$ against $1/T$ gives $A_4/A_5^{\frac{1}{2}} = 4.4 \times 10^5$ $(\text{litre mol}^{-1} \text{ s}^{-1})^{\frac{1}{2}}$, $E_4 - E_5/2 = 81.7 \pm 8 \text{ kJ mol}^{-1}$. If the present value of $k_5 = 2 \times 10^9$, independent of temperature, is accepted, $A_4 = 1.97 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $E_1 = 81.7 \pm 8 \text{ kJ mol}^{-1}$.

This work has been accepted for publication.

6. The decomposition of 2,2,3-trimethylbutane in the presence of oxygen

Although the strain in the central C-C bond in 2,2,3-trimethylbutane (TRIMB) is less than in 2,2,3,3-tetramethylbutane (TMB), it is still sufficient for the homolysis of the bond to be reasonably fast at about 500°C. As the $t\text{-C}_4\text{H}_9$ and $i\text{-C}_3\text{H}_7$ radicals produced predominantly react with O_2 to give the conjugate alkene and HO_2 , the following simple scheme forms the basis of the mechanism in KCl-coated vessels where HO_2 radicals are efficiently destroyed at the surface.



This simple mechanism gives the rate expression (x) exactly analogous to expression (i) obtained with TMB.

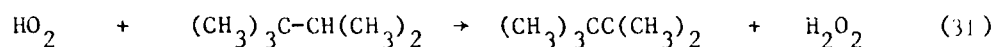
$$-d[\text{TRIMB}]/dt = k_{29}[\text{TRIMB}]^1[\text{O}_2]^0 \quad (\text{x})$$

Experimentally the rate is found to be zero order in O_2 , but the observed rate constant k_{obs} increases with the concentration of TRIMB because of the significant chain contribution from HO_2 and OH attack on TRIMB. By a double extrapolation of the observed rate constant k_{obs} to zero extent of reaction for a given initial concentration of TRIMB and to zero initial concentration of TRIMB, accurate values of k_{29} are obtained at 480°C and 500°C. Combination with Tsang's results²⁷ at higher temperatures then gives $\log_{10} (A_{29}/\text{s}^{-1}) = 16.46 \pm 0.12$ and $E_{29} = 305 \pm 1.5 \text{ kJ mol}^{-1}$ over the temperature range 480°-925°C. Combination of these parameters with those for reaction (-29) gives further information on the thermochemistry of $t\text{-C}_4\text{H}_9$ and $i\text{-C}_3\text{H}_7$ radicals, which has been the subject of considerable recent discussion. Table 16 gives the enthalpies of formation of $t\text{-C}_4\text{H}_9$ and $i\text{-C}_3\text{H}_7$ radicals together with the recommended values for CH_3 and C_2H_5 radicals.

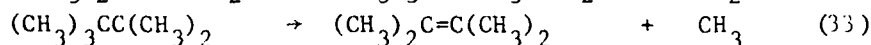
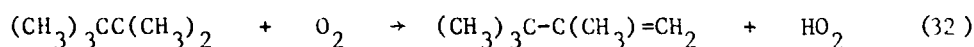
Table 16
Thermochemical values of alkyl radicals

R	$\Delta_f H_{298}^0 / \text{kJ mol}^{-1}$	$D_{298}^0(\text{R-H}) / \text{kJ mol}^{-1}$
CH_3	145.6 ± 1.0	438.4 ± 1.0
C_2H_5	118.0 ± 4.0	420.5 ± 4.0
$i\text{-C}_3\text{H}_7$	80.8 ± 4.0	402.5 ± 4.0
$t\text{-C}_4\text{H}_9$	37.6 ± 2.0	390.2 ± 2.0

From the variation of k_{obs} with the concentration of TRIMB, a preliminary estimate of $k_{31} = (3.1 \pm 0.6) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 500°C has been obtained.



Although *i*-butene and propene are the major initial products (ca. 80% initial yield), as predicted by the mechanism, 2,3,3-trimethylbut-1-ene is formed in about 15% yield together with smaller amounts of 2,3-dimethylbut-2-ene. From the variation in the relative yields of the two products with mixture composition, it has been established that they are formed in reactions (32) and (33).

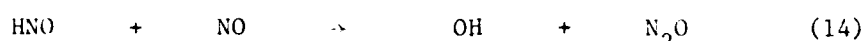
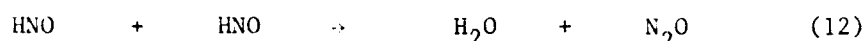
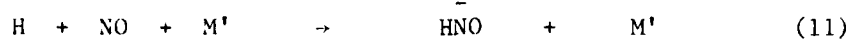
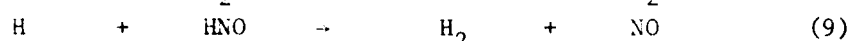
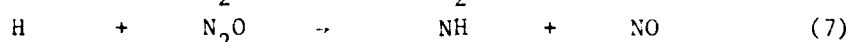
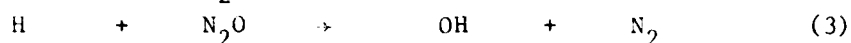
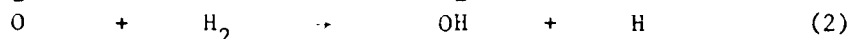


A value of $k_{33} = 1.4 \times 10^3$ at 500°C has been obtained, which is consistent with the rate constants for other 'strained' alkyl radical decomposition as shown in Table 8.

This work has now been published.²⁸

7. The reaction between hydrogen and nitrous oxide

The reaction between hydrogen and nitrous oxide has been studied mass spectrometrically at 500°C in a Pyrex vessel to confirm the mechanism below suggested by a study of the reaction at 600°C, and to obtain the activation energies of some of the reactions involved.

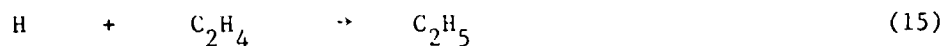


The behaviour of the reaction at 500°C is very similar to that at 600°C. Nitric oxide is formed as a minor product, reaching a maximum concentration and then decreasing as the reaction proceeds. The self-inhibition characteristics of the reaction are due to the marked retarding effect of nitric oxide on the reaction. Attention has been concentrated on the [NO], time profile for the mixture $[\text{N}_2\text{O}] = [\text{H}_2] = [\text{Ar}] = 100$ Torr and on the initial rates of nitrogen formation when small amounts of nitric oxide (0.1-5 Torr) are added to this mixture. This avoids the difficulties caused by uncertain coefficients for H_2 and Ar relative to N_2 as M in reaction (1) when the concentrations of the main reactants are varied.

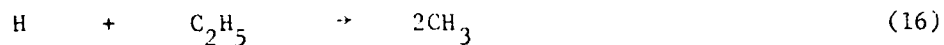
Use of a computer treatment already developed to interpret the results at 600°C shows that, as at 600°C, several combinations of rate constants will give a satisfactory interpretation of the results. Work is continuing to establish the best combination of rate constants and to use the computer program to examine what experiments might provide further information on this system.

Some studies have been made involving the addition of ethane to slowly

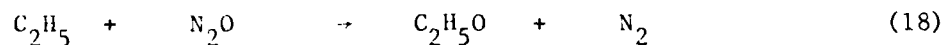
reacting mixtures of $H_2 + N_2O$ at $550^{\circ}C$ with the intention of using the system as a source of H and OH radicals in the absence of O_2 . The major product initially is ethylene, but it rapidly reaches a steady concentration, probably due mainly to the equilibrium (15).



Once equilibrium has been established, methane becomes the major product and the kinetic features of the reaction suggest that it is produced by reactions (16) and (17).



It was hoped that alkoxy radicals might be produced by reaction (18), so that their behaviour could be investigated, but no evidence for this reaction has been found.



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Conferences attended and Lectures presented

Dr. Walker attended the "Fifth International Symposium on Gas Kinetics", held in Manchester in July 1977 and presented a paper entitled "The Decomposition of Tetramethylbutane in the Presence of Oxygen".

Professor Baldwin gave an invited lecture entitled "Problems and Progress in Hydrocarbon Oxidation", at the Autumn meeting of the Chemical Society, held at the University of Aberdeen in September 1977.

Professor Baldwin and Dr. Walker attended the Seventeenth (International) Combustion Symposium held at the University of Leeds in August 1978, and presented a paper entitled "Rate Constants for Reactions of HO_2 Radicals with Alkanes, Aldehydes, and Related Compounds".

Dr. Walker attended the U.S. Air Force Contractors' Meeting held at Dayton, Ohio, in October 1978, and presented a paper entitled "Rate Constants for H, OH, and HO_2 Radical Attack on Alkanes".

Professor Baldwin, Dr. Walker, and their research group attended a one-day research meeting on "Combustion" at the University of York in May 1979.

Professor Baldwin and Dr. Walker presented a paper entitled "Towards a Quantitative Interpretation of Gas-Phase Hydrocarbon Oxidation", at the meeting of the Gas Kinetics Discussion Group of the Chemical Society at Keele University in September 1979.

Professor Baldwin attended the U.S. Air Force Contractors' Meeting on "Air-Breathing Combustion Dynamics and Kinetics" held in Alexandria, Virginia, in January 1980, where he presented a paper entitled "Kinetics of Oxidation Reactions".

Dr. Walker attended the "Sixth International Symposium on Gas Kinetics" held at Southampton in July 1980, and presented a paper entitled "Elementary Reactions in the Gas-Phase Oxidation of Alkenes".

Professor Baldwin and Dr. Walker presented a paper entitled "Elementary Reactions in the Oxidation of Alkenes" at the Eighteenth (International) Combustion Symposium held at the University of Waterloo, Canada, in August 1980.

Professor Baldwin presented a paper entitled "Elementary Steps in the Oxidation of Alkanes and Alkenes" at a Seminar on Combustion Phenomena held at the Ballistic Research Laboratory near Aberdeen, Maryland, in August 1980.

Professor Baldwin and Dr. Walker gave the Christmas Schools Lecture entitled "Combustion: Some Burning Problems" at Sheffield in December 1980.

Professor Baldwin gave an invited talk on "Dual Sensitising and Inhibiting Action of Additives in Chain Reactions" at a one-day Symposium on Combustion held at the University of Manchester Institute of Science and Technology in July 1981.

Dr. Walker has been invited to give a paper on "Recent Progress in Gas-phase Hydrocarbon Oxidation Chemistry" at a two-day meeting of the Gas Kinetics Discussion Group of the Faraday Division of the Royal Society of Chemistry. Professor Baldwin will present a paper entitled "Interaction of Homogeneous and Heterogeneous Chain Termination" at the same meeting, which will be held at the University of Hull in September 1981.

* * * * *

Personnel

Mrs. J. P. Bennett, who was financed under Grant AFOSR 73-2450, has successfully submitted for the Ph.D. degree.

Mr. R. W. Walker, financed by a Science Research Council Award, who joined the group in September 1975, has completed his period of study and has successfully submitted his Ph.D. thesis. He has now taken up a position with Imperial Chemical Industries Ltd.

Mr. G. A. Evans, who joined the research group in 1975, and was financed under Grants AFOSR 73-2450 and AFOSR 77-3215, has completed his period of study and has submitted his Ph.D. thesis.

Mr. A. P. Keen (B.Sc., Hull 1977) joined the group in September 1977, financed by Grant AFOSR 77-3215, and completed his period of study in July 1980.

Mr. I. A. Pickering (B.Sc., Hull 1978) who joined the research group as technician in July 1978, took up another appointment in January 1980. Miss P. Theakstone was appointed as a replacement in September 1980.

Mr. D. G. Malcolm (B.Sc., Hull 1978) and Mr. M.W.M. Hisham (B.Sc., University of Sri Lanka) joined the research group in September 1978 and were financed by Grant AFOSR 77-3215. Mr. Malcolm has taken up the post of Research Assistant, financed by the Science Research Council, as from October 1979.

Miss A. Sutcliffe (B.Sc., Hull 1979) joined the research group in September 1979 and is financed under Grant AFOSR 77-3215.

Mr. D. R. Stout (B.Sc., 1980) joined the group in October 1980 and is financed under Grant AFOSR 77-3215.

Mr. G. R. Drewery (B.Sc., Hull 1980) joined the group in September 1980, and is financed by a Science Research Council Award.

Mr. C. J. Cleugh, who was financed by the Science Research Council, has been awarded the degree of M.Sc.

Dr. R. W. Walker has been promoted to a Readership with effect from 1st October 1980.

The Science Research Council have made a grant of £33,050 to Professor Baldwin and Dr. Walker for the purchase of Perkin Elmer gas chromatographic equipment, and to provide for a Research Assistant. Further

grants of £6,394 and £24,500 have recently been made for further gas chromatographic equipment, and a three-year Research Assistantship, respectively.

Informal discussions have taken place with Professor Barnard of the University of Sheffield, Professor Ashmore, Dr. Simmons and Dr. Tyler of the University of Manchester Institute of Science and Technology, Professor Gray, Professor Williams, Professor Dixon-Lewis, Dr. Baulch, and Dr. Griffiths of Leeds University, Dr. L. Batt of Aberdeen University, Dr. Golden of the Stanford Research Institute, Professor Waddington of York University, Dr. Turner of Bradford University, Dr. D. Booth of Newcastle Polytechnic, Dr. Cohen of Drexel University, Professor Glassman and Dr. Dryer of Princeton University, Dr. K. Booth of Imperial Chemical Industries Ltd., Dr. N. Cohen of the Aerospace Corporation, and Dr. J. M. Heimerl of the Army Ballistics Laboratory.

Appendix I

Rate Constants for the i-C₄H₉ Radical System at 480°C

	Reaction	k/dm ³ ,mol,s	note
CH ₃ CH(CH ₃)CH ₂	→ C ₃ H ₆ + CH ₃	8.8 × 10 ⁴	
CH ₃ CH(CH ₃)CH ₂ + O ₂	→ i-C ₄ H ₈ + HO ₂	6.8 × 10 ⁷	
CH ₃ CH(CH ₃)CH ₂ + O ₂	→ CH ₃ CH(CH ₃)CH ₂ O ₂	1.0 × 10 ⁹	a
CH ₃ CH(CH ₃)CH ₂ O ₂	→ CH ₃ CH(CH ₃)CH ₂ + O ₂	2.6 × 10 ⁶	b
CH ₃ CH(CH ₃)CH ₂ O ₂	→ CH ₃ CH(CH ₂ OOH)CH ₂	4.45 × 10 ⁴	b
CH ₃ CH(CH ₂ OOH)CH ₂	→ CH ₃ CH(CH ₃)CH ₂ O ₂	1.35 × 10 ⁶	b
CH ₃ CH(CH ₃)CH ₂ O ₂	→ CH ₃ C(CH ₃)(CH ₂ OOH)	1.83 × 10 ⁵	b
CH ₃ C(CH ₃)(CH ₂ OOH)	→ CH ₃ CH(CH ₃)CH ₂ O ₂	8.3 × 10 ⁵	b
CH ₃ CH(CH ₂ OOH)CH ₂	→ 3-methyloxetan + OH	(1-2) × 10 ⁶	c
CH ₃ C(CH ₃)(CH ₂ OOH)	→ isobutene oxide + OH	1.8 × 10 ⁶	c
CH ₃ CH(CH ₂ OOH)CH ₂ + O ₂	→ CH ₃ CH(CH ₂ OOH)CH ₂ O ₂	1.0 × 10 ⁹	a
CH ₃ CH(CH ₂ OOH)CH ₂ O ₂	→ CH ₃ CH(CH ₂ OOH)CH ₂ + O ₂	2.6 × 10 ⁶	b
CH ₃ C(CH ₃)(CH ₂ OOH) + O ₂	→ CH ₃ C(CH ₃)(CH ₂ OOH)O ₂	1.0 × 10 ⁹	a
CH ₃ C(CH ₃)(CH ₂ OOH)O ₂	→ CH ₃ C(CH ₃)(CH ₂ OOH) + O ₂	7.5 × 10 ⁶	b
CH ₃ CH(CH ₂ OOH)CH ₂ O ₂	→ CH ₃ CHO + 2HCHO + OH	(1-2) × 10 ⁶	c
CH ₃ C(CH ₃)(CH ₂ OOH)O ₂	→ CH ₃ COCH ₃ + HCHO + HO ₂	3.0 × 10 ⁶	c
CH ₃ C(CH ₃)(CH ₂ OOH)	→ CH ₂ =C(CH ₃)CH ₂ OH + OH	1.3 × 10 ⁵	c
CH ₃ C(CH ₃)(CH ₂ OOH)	→ CH ₂ =C(CH ₃)CHO + OH + H ₂	1.3 × 10 ⁵	c
CH ₃ C(CH ₃)(CH ₂ OOH)	→ (CH ₃) ₂ CHCHO + OH	4.2 × 10 ⁵	c

a Assumed value.

b The values are dependent on the calculated value of K(R + O₂).

c The values are determined from maximum and minimum limits.

Appendix II

Rate Constants for the Oxidation of Pentane at 480°C

<u>Reaction</u>		<u>k/s⁻¹</u>	<u>note</u>
CH ₃ CH ₂ CHCH ₂ CH ₃	→ CH ₃ CH ₂ CH=CH ₂ + CH ₃	1.6 × 10 ⁵	
CH ₃ CHCH ₂ CH ₂ CH ₃	→ CH ₃ CH=CH ₂ + C ₂ H ₅	2.3 × 10 ⁵	
CH ₃ CH(O ₂)CH ₂ CH ₂ CH ₃	→ CH ₃ CH(OOH)CHCH ₂ CH ₃	4.7 × 10 ⁴	
CH ₃ CH(O ₂)CH ₂ CH ₂ CH ₃	→ CH ₃ CH(OOH)CH ₂ CHCH ₃	3.0 × 10 ⁵	
CH ₃ CH(OOH)CH ₂ CHCH ₃	→ 2,4-dimethyloxetan + OH	1.0 × 10 ⁶	b
CH ₃ CH(OOH)CH ₂ CH(O ₂)CH ₃	→ 2CH ₃ CHO + HCHO + OH	5 × 10 ⁵	b
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ + O ₂	→ CH ₃ CH ₂ CH ₂ CH=CH ₂ + HO ₂	2.9 × 10 ⁸	a
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ O ₂	→ CH ₃ CHCH ₂ CH ₂ CH ₂ OOH	6.6 × 10 ⁵	
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ O ₂	→ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OOH	9.3 × 10 ⁴	
CH ₃ CH ₂ CHCH ₂ CH ₂ OOH	→ 2-ethyloxetan + OH	1.0 × 10 ⁶	b
CH ₃ CH ₂ CH(O ₂)CH ₂ CH ₂ OOH	→ C ₂ H ₅ CHO + 2HCHO + OH	8 × 10 ⁵	b

a Units, dm³ mol⁻¹ s⁻¹.

b Values determined from maximum and minimum limits.